Molecular Structure of Salicylic Acid and its Hydrates: A Rotational Spectroscopy Study

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Determination of the θ angle

For monohydrated complexes with a planar or nearly planar structure, in which the *ab* inertial plane roughly overlaps with the same inertial plane of the monomer form, Ouyang and Howard [31] developed a method in order to determine the angle θ between the *a* principal axis of the monomer form and the intermolecular axis of the cluster using the next expression:

$$\sin^2\theta = \frac{I_A(\mu R_{CM}^2 + I_a + I_b - I_A) - I_a(\mu R_{CM}^2 + I_b)}{\mu R_{CM}^2(I_b - I_a)} \qquad (1)$$

where I_A, I_B and I_C are the principal moments of inertia of the monohydrated complex while I_a, I_b and I_c are those of the monomer form, μ is the reduced mass considering a pseudo-diatomic model and R_{CM} is the distance between the centers of mass of the monomer and the water molecule in the complex. R_{CM} could be taken from the geometrical predictions or calculated by the equation:

$$R_{CM}^2 = \frac{(I_C - I_c)}{\mu} \qquad (2)$$

Figure S1. CP-FTMW, 2-8 GHz, rotational spectrum of SA and its water complexes (upper figure). At the bottom, a zoom of the spectrum form 6-8 GHz is shown, where the intensities of the most intense transitions of the SA-I and SA-w (SA-I-w-a) species can be compared. The a) excerpt shows the $4_{0,4} \leftarrow 3_{1,3}$ transition for the SA-I ^{13}C isotopologues. (See Figure 3 for the atom labelling).
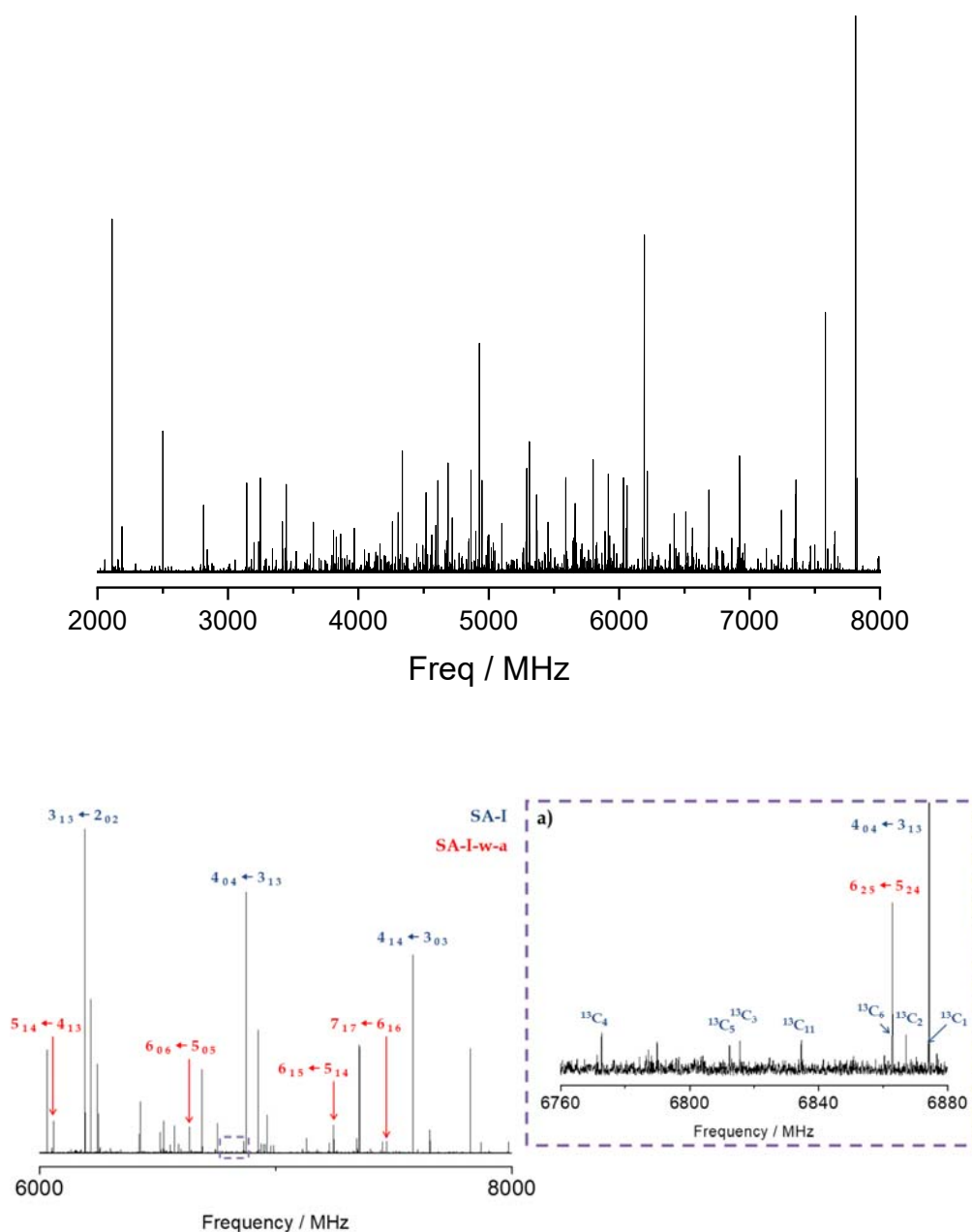
Figure S2. Stable conformers predicted for salicylic acid monomer. Their corresponding parameters are given in Table S1. Relative energies to conformer I are predicted at B3LYP-D3-6-311++G(d,p) level.

I	II	III	IV	V
0.0 cm^{-1}	1144.6 cm^{-1}	3365.1 cm^{-1}	3786.0 cm^{-1}	3913.2 cm^{-1}
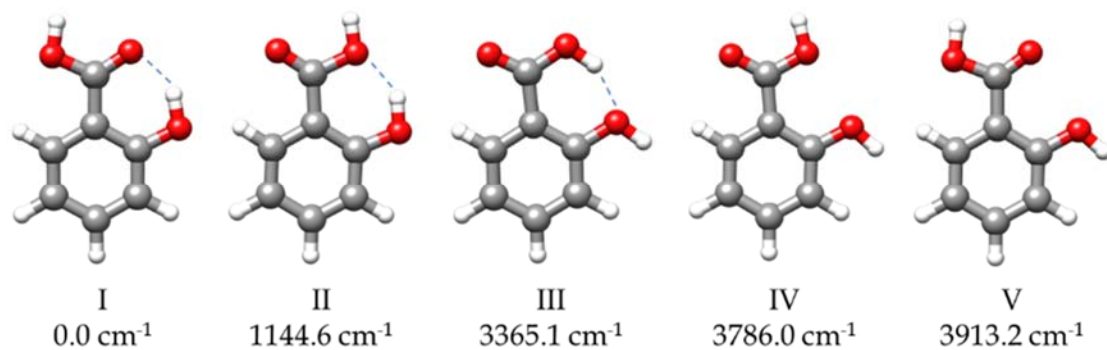
Figure S3. Stable conformers predicted for the monohydrated complex of salicylic acid. Their corresponding parameters are given in Table S2. Relative energies to conformer I-w-a are predicted at B3LYP-D3-6-311++G(d,p) level.

I-w-a
0.0 cm^{-1}

I-w-b
2030.8 cm^{-1}

I-w-c
2657.1 cm^{-1}

I-w-d
2757.4 cm^{-1}

II-w-a
890.6 cm^{-1}

II-w-b
3033.8 cm^{-1}

II-w-c
3311.3 cm^{-1}

II-w-d
3805.0 cm^{-1}

III-w-a
3735.0 cm^{-1}

III-w-b
4783.7 cm^{-1}

III-w-c
5002.3 cm^{-1}

III-w-d
5056.0 cm^{-1}

IV-w
5558.3 cm^{-1}
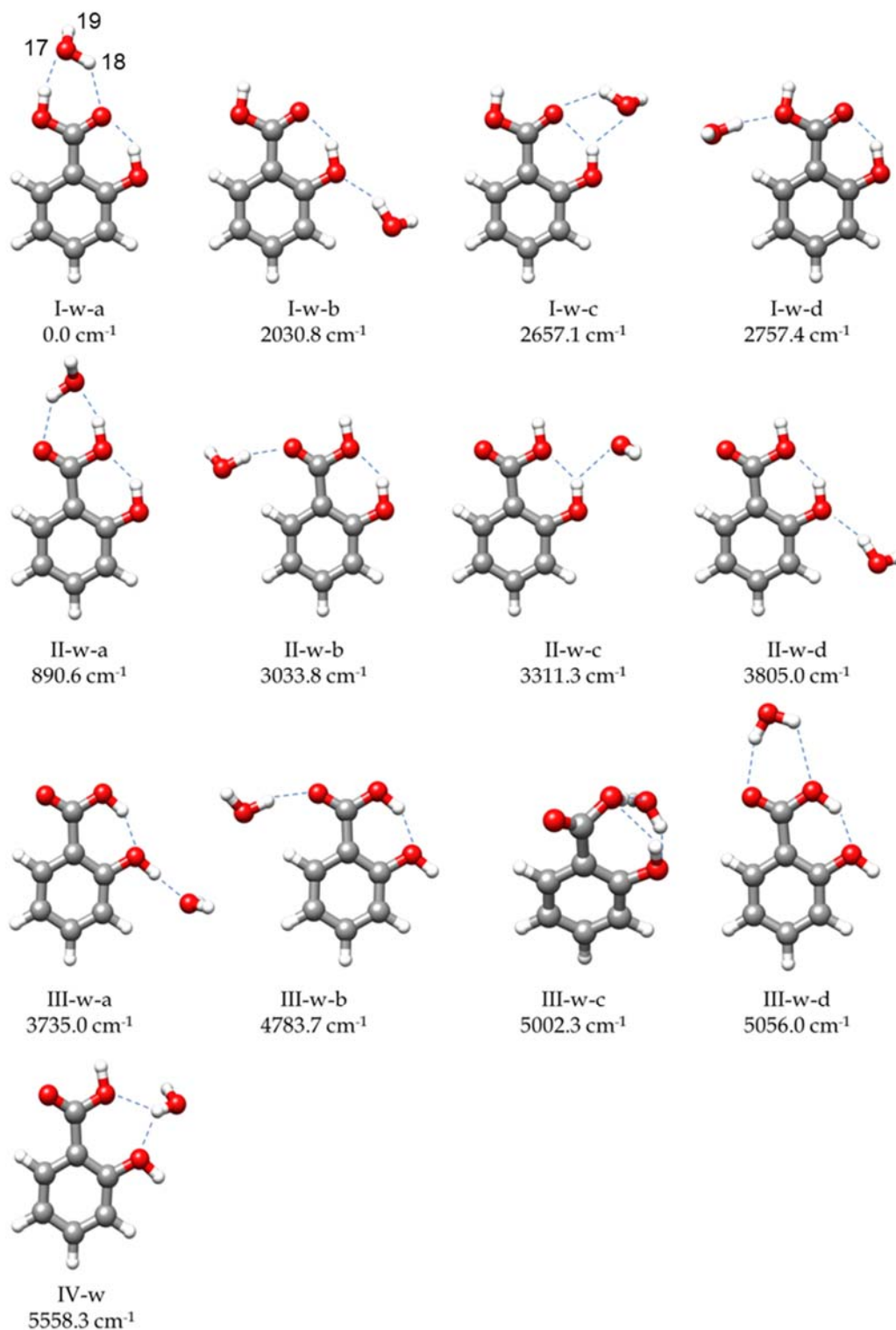
Figure S4. Stable conformers predicted for the dihydrated complex of salicylic acid. The parameters for the first-row conformers are given in Table S3. Relative energies to conformer I-w₂-a are predicted at B3LYP-D3-6-311++G(d,p) level.

I-w$_2$-a
0.0 cm^{-1}

II-w$_2$-a
693.9 cm^{-1}

I-w$_2$-ab
2401.6 cm^{-1}

III-w$_2$-a
3575.7 cm^{-1}

I-w2-ph
3291 cm^{-1}

III-w2-ph
4543 cm^{-1}
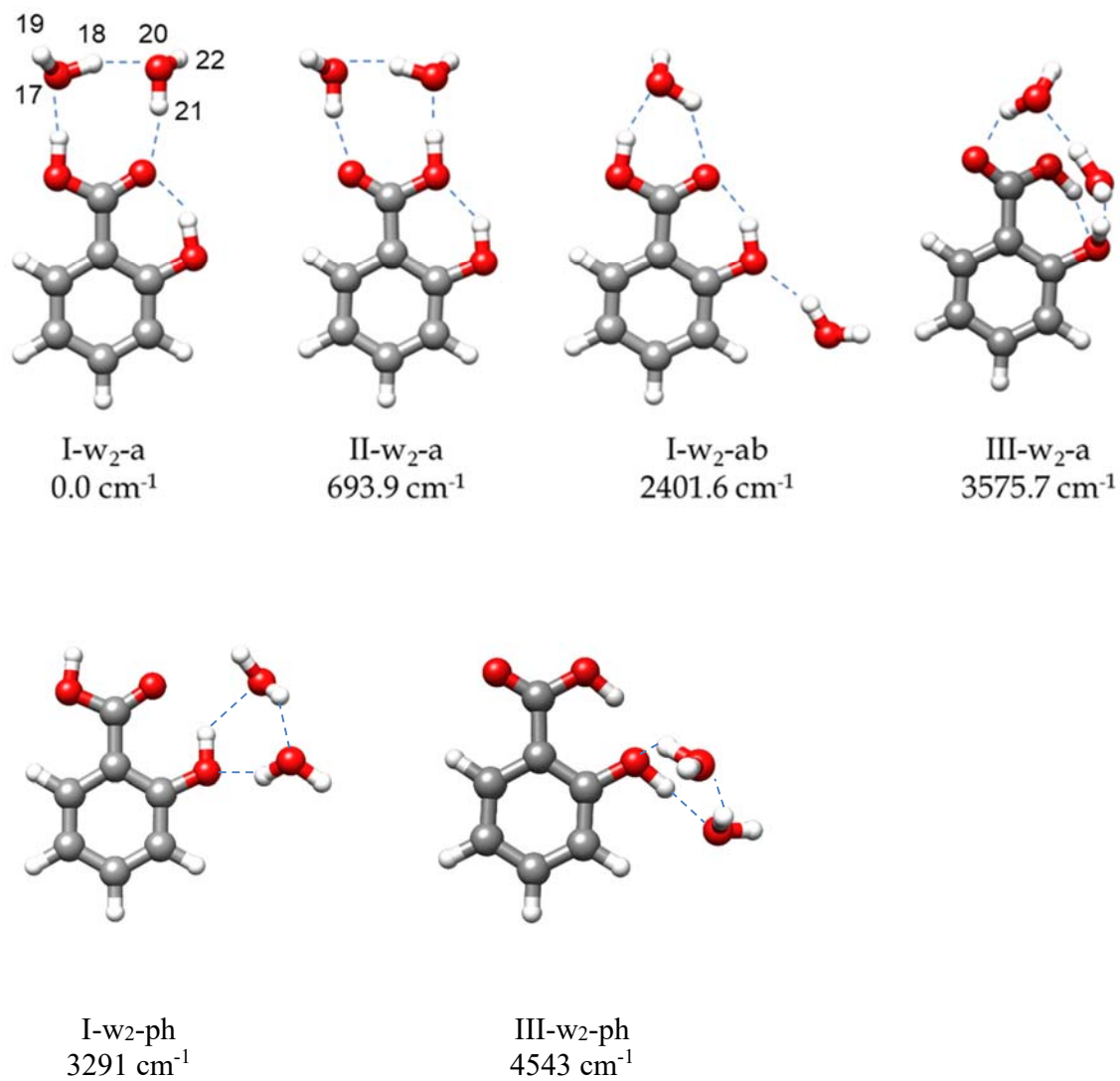
Figure S5. Stable conformers predicted for the trihydrated complex of salicylic acid. The parameters are given in Table S4. Relative energies to conformer I-w₃-a are predicted at B3LYP-D3/6-311++G(d,p) level.

I-w₃-a
0.0 cm⁻¹

I-w₃-b
130.4 cm⁻¹

I-w₃-c
130.4 cm⁻¹

I-w₃-d
378.2 cm⁻¹

II-w₃-a
575.6 cm⁻¹

I-w₃-e
846.4 cm⁻¹

I-w₃-ph
3215 cm⁻¹

III-w₃-ph
3162 cm⁻¹
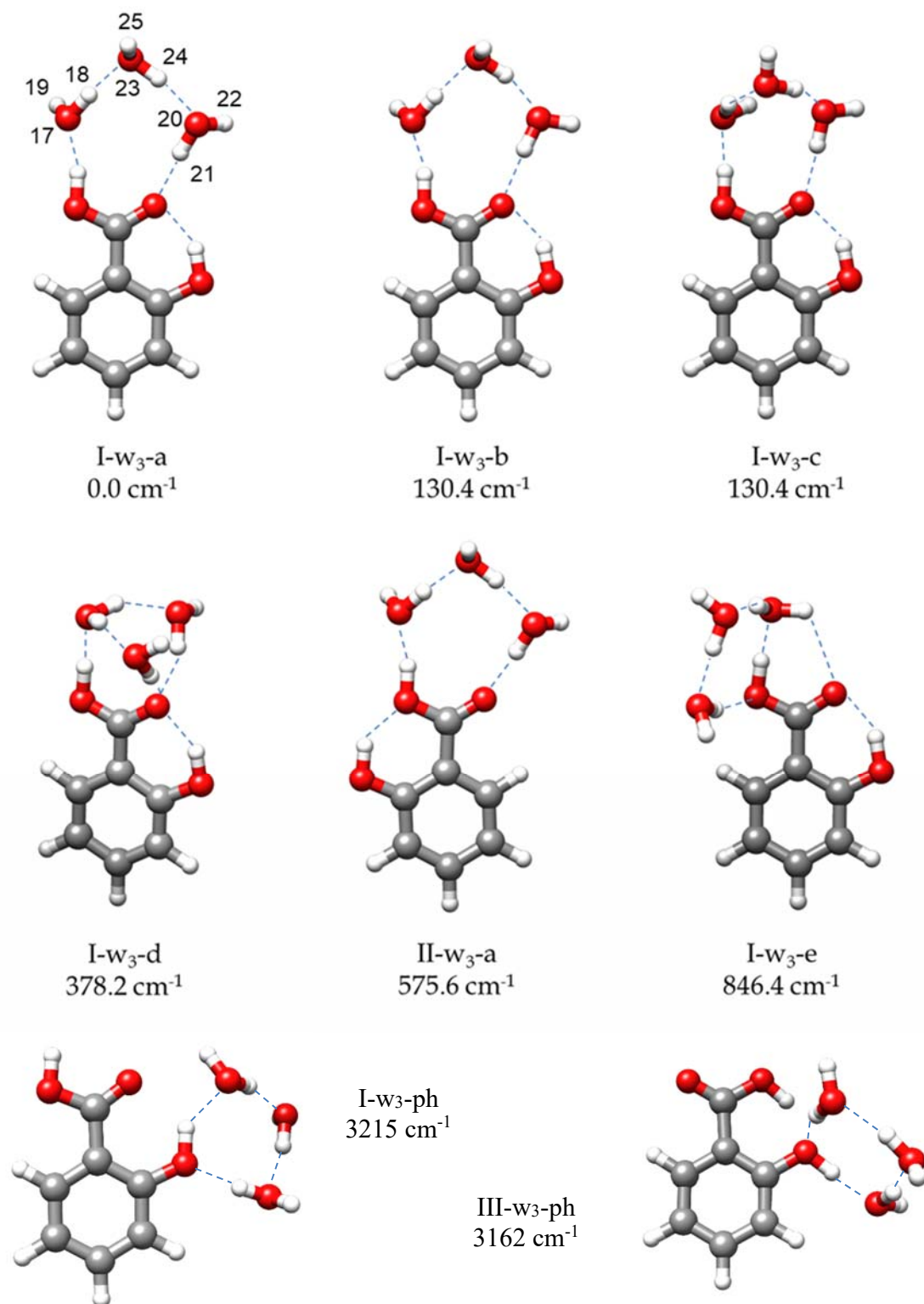
Figure S6. Stable conformers predicted for the tetrahydrated complex of salicylic acid. Their corresponding parameters are given in Table S 5. Relative energies to conformer I-w$_4$-a are predicted at B3LYP-D3/6-311++G(d,p) level.

I-w$_4$-a
0.0 cm^{-1}

I-w$_4$-b
165.7 cm^{-1}

I-w$_4$-c
241.2 cm^{-1}

I-w$_4$-d
267.8 cm^{-1}

I-w$_4$-e
269.6 cm^{-1}

I-w$_4$-f
336.5 cm^{-1}

I-w$_4$-g
509.7 cm^{-1}

II-w$_4$-a
535.3 cm^{-1}

I-w$_4$-h
591.6 cm^{-1}

Figure S7. a) Bond Critical Points (BCPs) and Ring Critical Points (RCPs) in yellow, and the Bond Paths (BPs) in orange calculated at B3LYP-D3/6-311++G(d,p) level for the conformer I of salicylic acid from the Quantum Theory of "atoms in molecules" (QTAIM) analyses. b) Results of Non-Covalent Interaction (NCI) analysis. Each point in the scatter graph corresponds to a grid point in 3D space and represents the reduced density gradient (RDG) vs. sign[$\lambda_2(r)$]$\rho(r)$. The blue-green spikes in the left (negative side) corresponds to attractive interactions, while those orange-red spikes in the right (positive side) corresponds to negative interactions. The points corresponding to low RDG values represent weak interactions. Those with RDG<0.5 a.u. are represented by the isosurface.
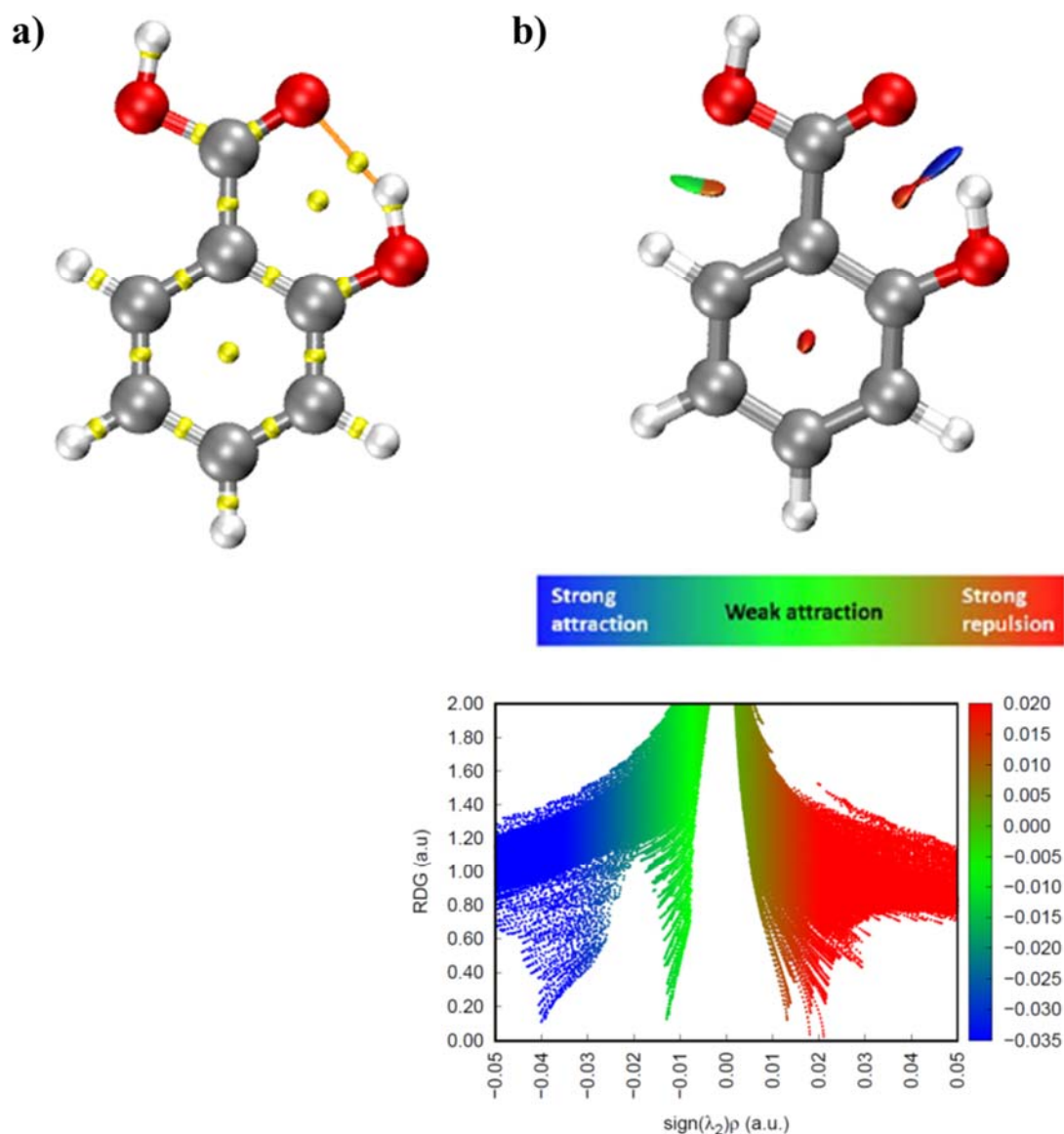
Figure S8. a) Bond Critical Points (BCPs) and Ring Critical Points (RCPs) in yellow, and the Bond Paths (BPs) in orange calculated at B3LYP-D3/6-311++G(d,p) level for the conformer I-w-a of salicylic acid – water complex from the Quantum Theory of "atoms in molecules" (QTAIM) analyses. b) Results of Non-Covalent Interaction (NCI) analysis. Each point in the scatter graph corresponds to a grid point in 3D space and represents the reduced density gradient (RDG) vs. sign$[\lambda_2(r)]\rho(r)$. The blue-green spikes in the left (negative side) corresponds to attractive interactions, while those orange-red spikes in the right (positive side) corresponds to negative interactions. The points corresponding to low RDG values represent weak interactions. Those with RDG<0.5 a.u. are represented by the isosurface.
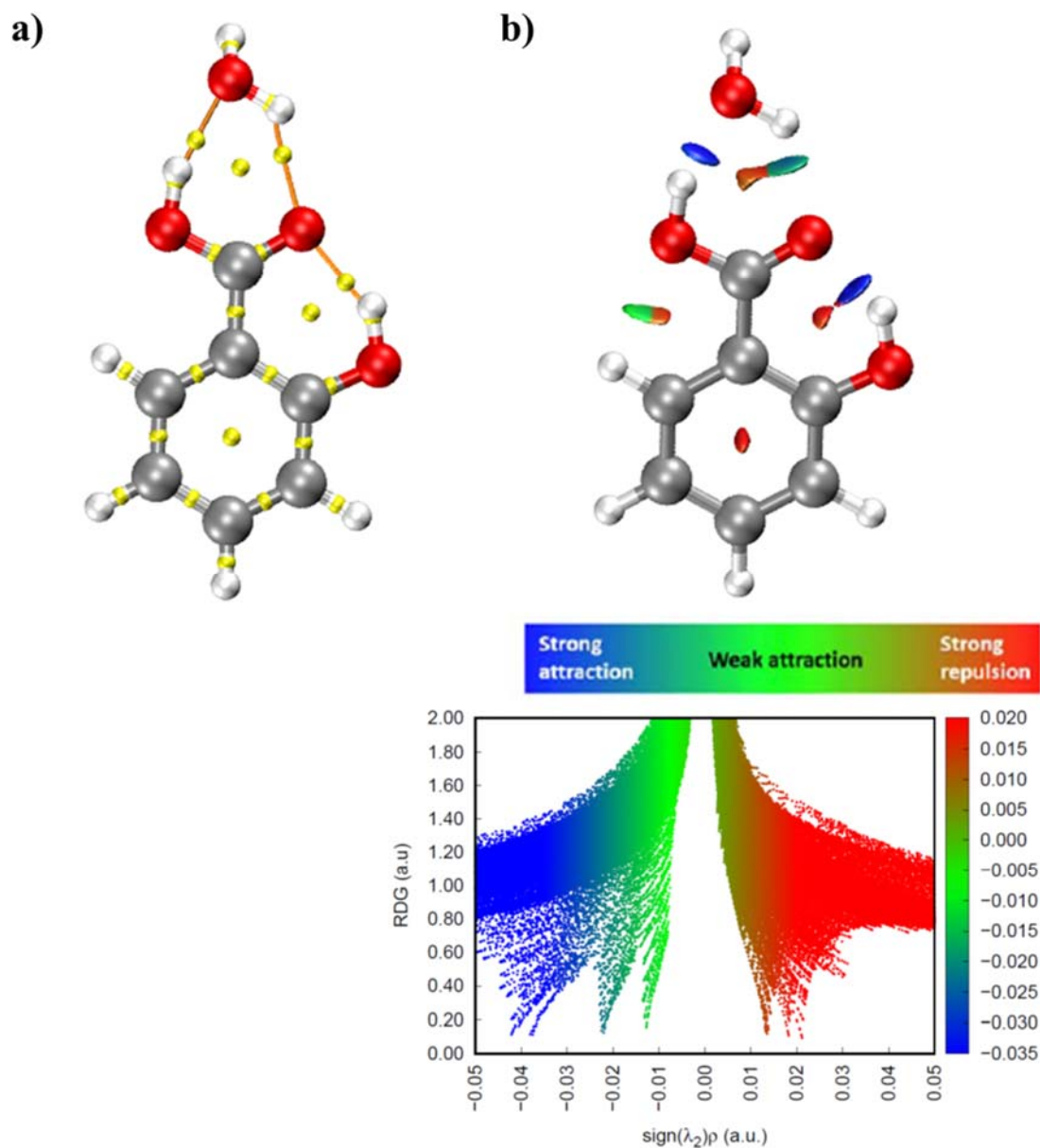
Figure S9. a) Bond Critical Points (BCPs) and Ring Critical Points (RCPs) in yellow, and the Bond Paths (BPs) in orange calculated at B3LYP-D3/6-311++G(d,p) level for the conformer I-w$_2$-a of salicylic acid – water$_2$ complex from the Quantum Theory of "atoms in molecules" (QTAIM) analyses. b) Results of Non-Covalent Interaction (NCI) analysis. Each point in the scatter graph corresponds to a grid point in 3D space and represents the reduced density gradient (RDG) vs. sign[$\lambda_2(r)$]$\rho(r)$. The blue-green spikes in the left (negative side) corresponds to attractive interactions, while those orange-red spikes in the right (positive side) corresponds to negative interactions. The points corresponding to low RDG values represent weak interactions. Those with RDG<0.5 a.u. are represented by the isosurface.
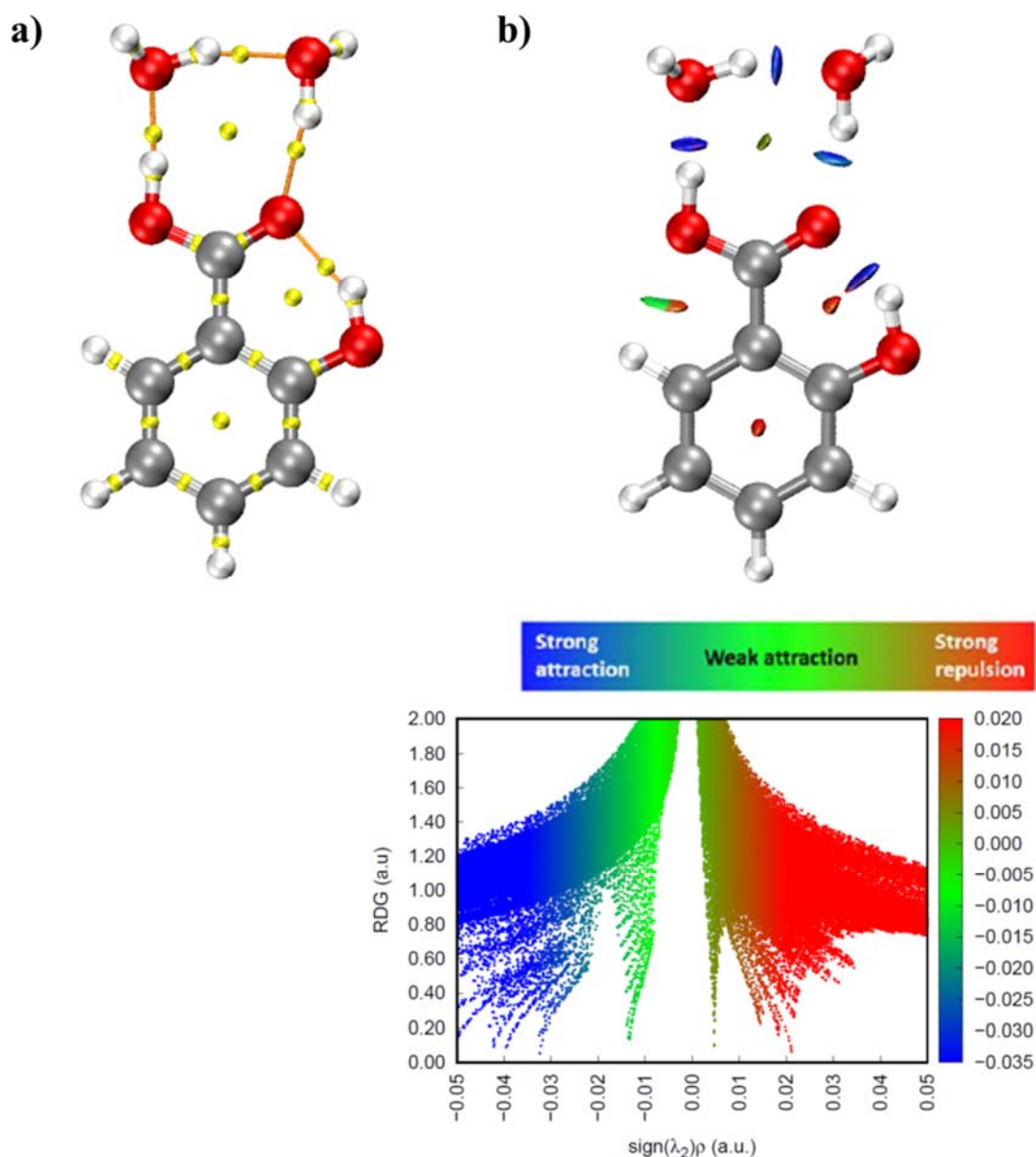
Figure S10. a) Bond Critical Points (BCPs) and Ring Critical Points (RCPs) in yellow, and the Bond Paths (BPs) in orange calculated at B3LYP-D3/6-311++G(d,p) level for the conformer I-w_3-a of salicylic acid – water$_3$ complex from the Quantum Theory of "atoms in molecules" (QTAIM) analyses. b) Results of Non-Covalent Interaction (NCI) analysis. Each point in the scatter graph corresponds to a grid point in 3D space and represents the reduced density gradient (RDG) vs. sign[$\lambda_2(r)$]$\rho(r)$. The blue-green spikes in the left (negative side) corresponds to attractive interactions, while those orange-red spikes in the right (positive side) corresponds to negative interactions. The points corresponding to low RDG values represent weak interactions. Those with RDG<0.5 a.u. are represented by the isosurface.

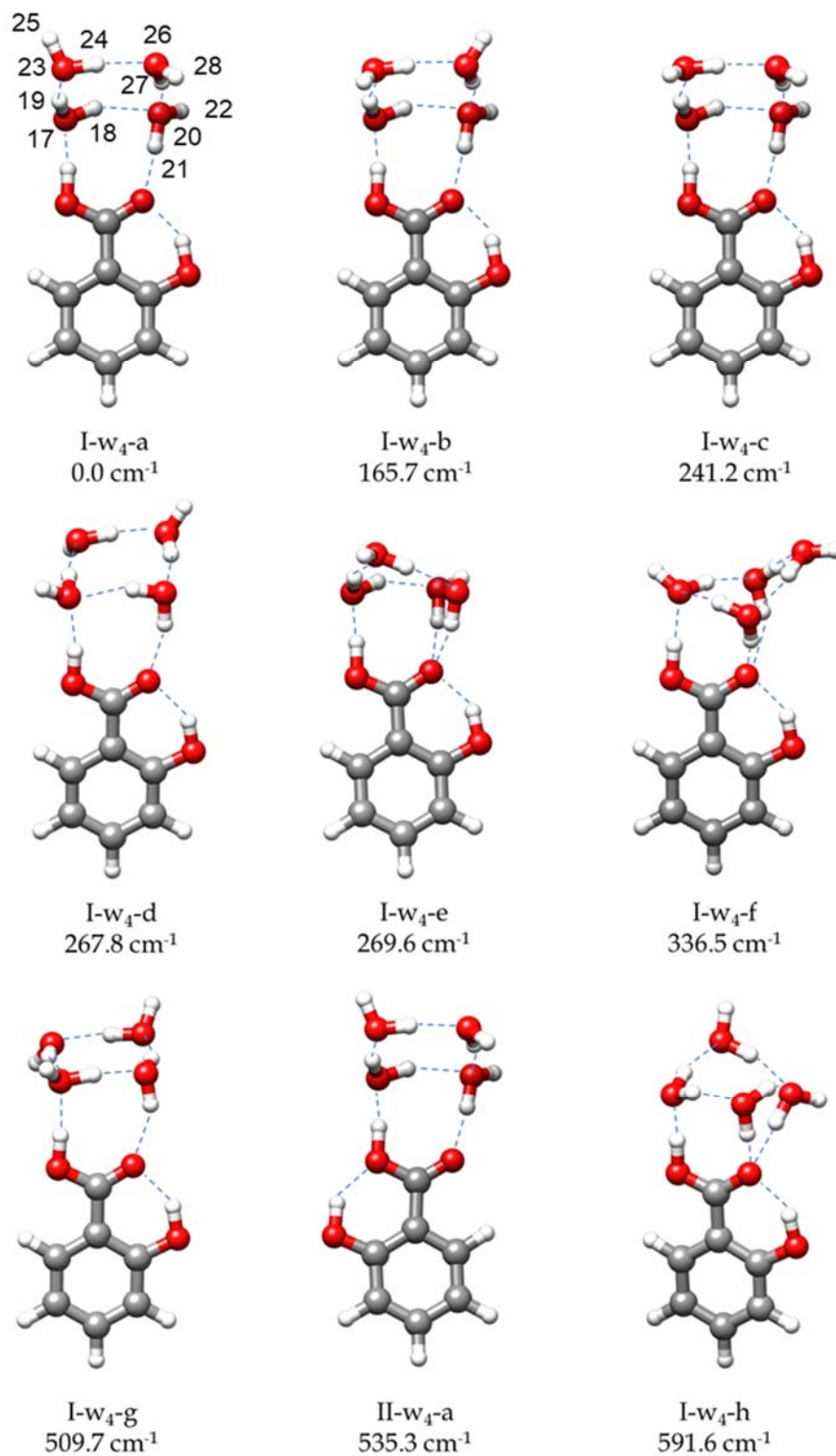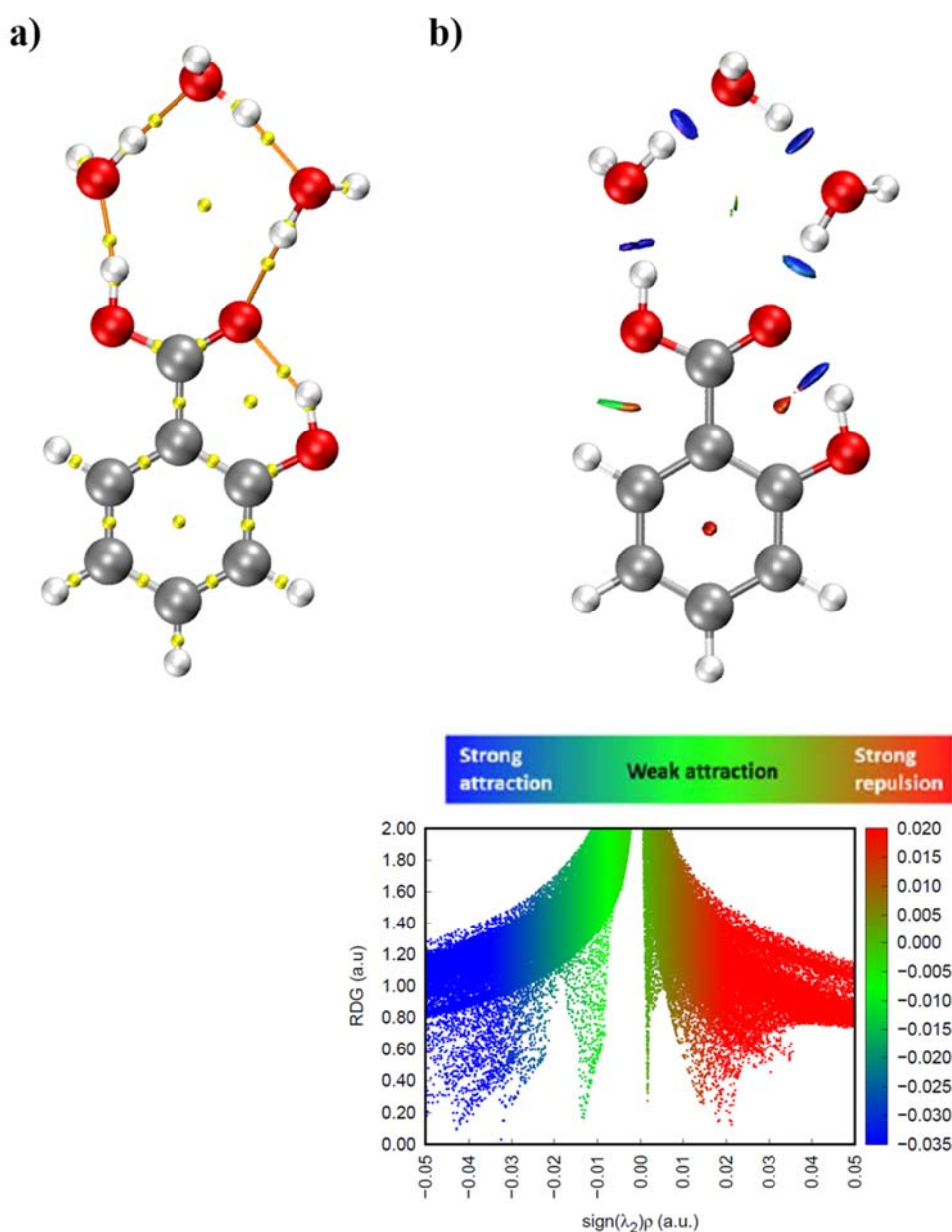**Figure S11.** a) Bond Critical Points (BCPs) and Ring Critical Points (RCPs) in yellow, and the Bond Paths (BPs) in orange calculated at B3LYP-D3/6-311++G(d,p) level for the conformer I-w$_4$-a of salicylic acid – water$_4$ complex from the Quantum Theory of "atoms in molecules" (QTAIM) analyses. b) Results of Non-Covalent Interaction (NCI) analysis. Each point in the scatter graph corresponds to a grid point in 3D space and represents the reduced density gradient (RDG) vs. sign[$\lambda_2(r)]\rho(r)$. The blue-green spikes in the left (negative side) corresponds to attractive interactions, while those orange-red spikes in the right (positive side) corresponds to negative interactions. The points corresponding to low RDG values represent weak interactions. Those with RDG<0.5 a.u. are represented by the isosurface. The hydrogen bond between the O-H···Ow$_1$ presents a sign[$\lambda_2(r)]\rho(r)$ value close to -0.007 a.u., associated to a strong interaction.
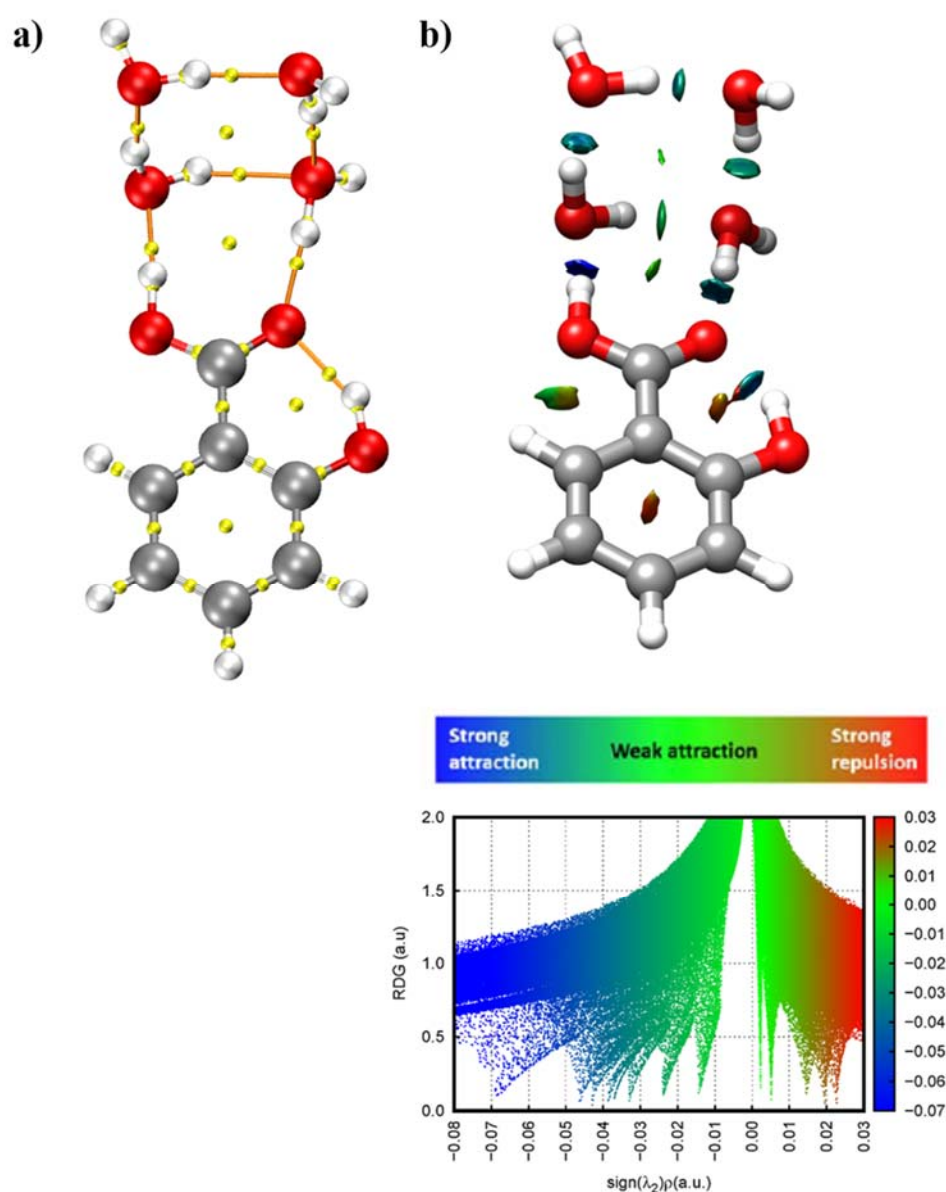
Figure S12. Possible path for inversion for the conformer I-w3-a. It was calculated in two steps by scanning successively the flipping angles α and β. Through this path small potential energy barriers allow the interconversion between two equivalent forms. Calculations have been done at B3LYP-D3/6-311++G(d,p) level of theory.
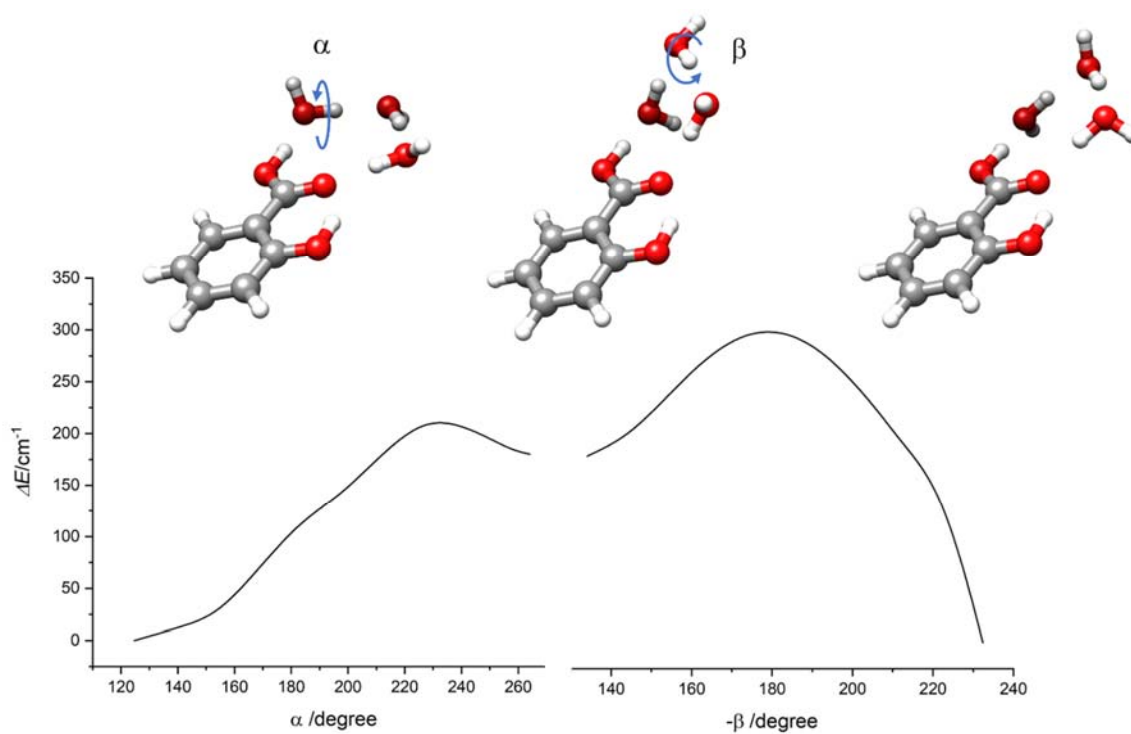
Table S1. Rotational parameters predicted from B3LYP-D3/6-311++G(d,p) level of theory for the most stable species of salicylic acid monomer.

Parameter [a]	I	II	III	IV	V
A/MHz	2336.06	2329.26	2322.93	2318.42	2295.69
B/MHz	1221.82	1211.10	1208.39	1205.87	1210.29
C/MHz	802.23	796.80	795.29	793.85	792.49
P_{cc}/uÅ^2	0.00	0.00	0.16	0.23	0.00
μ_a/D	-0.4	-0.1	5.7	2.8	2.4
μ_b/D	2.2	-0.7	3.7	2.2	-1.9
μ_c/D	0.0	0.0	0.3	0.1	0.0
ΔE_{DFT}/cm^{-1}	0.0 [b]	1144.6	3365.1	3786.0	3913.2

[a] A, B and C are the rotational constants. P_{cc} is the planar moment of inertia, derived from $P_{cc}=(I_a+I_b-I_c)/2$. μ_a, μ_b and μ_c are the components of the electric dipole moment. ΔE is the energy relative to predicted global minimum conformer.

[b] Absolute energy is -496.2168409 E_h.

Table S2. Rotational parameters predicted at B3LYP-D3/6-311++G(d,p) level of theory for the stable conformers of the monohydrated complex of the salicylic acid.

Parameter[a]	I-w-a	II-w-a	I-w-b	I-w-c	I-w-d
A/MHz	2313.15	2311.93	1399.25	1581.85	1335.12
B/MHz	648.76	647.51	821.10	805.29	870.84
C/MHz	507.09	506.29	517.80	534.31	537.91
P_{cc}/u$Å^2$	0.42	0.44	0.33	0.60	9.67
μ_a/D	-0.6	-0.7	-2.5	0.4	0.3
μ_b/D	1.0	-0.6	0.5	2.0	0.6
μ_c/D	-1.2	1.2	0.9	1.3	1.1
ΔE_{DFT}/cm^{-1}	0.0 [b]	890.6	2030.8	2657.1	2757.4
	II-w-b	**II-w-c**	**III-w-a**	**II-w-d**	**III-w-b**
A/MHz	1355.92	1379.21	1223.98	1527.73	1348.17
B/MHz	868.96	816.33	842.59	790.54	878.31
C/MHz	529.99	513.19	516.33	522.23	532.79
P_{cc}/u$Å^2$	0.37	0.37	16.95	1.18	0.85
μ_a/D	-0.6	0.4	9.4	1.7	6.2
μ_b/D	1.8	-1.3	1.7	-2.8	-0.5
μ_c/D	1.0	-1.1	0.2	0.0	1.0
ΔE_{DFT}/cm^{-1}	3033.8	3311.3	3735.0	3805.0	4783.7
	III-w-c	**III-w-d**	**IV-w**		
A/MHz	1361.27	2276.47	1425.13		
B/MHz	968.06	605.99	836.89		
C/MHz	688.29	478.71	549.88		
P_{cc}/u$Å^2$	79.53	0.13	19.71		
μ_a/D	3.3	9.3	2.3		
μ_b/D	-4.0	3.6	-1.6		
μ_c/D	2.3	0.2	0.8		
ΔE_{DFT}/cm^{-1}	5002.3	5056.0	5558.3		

[a] See footnote of Table S1.

[b] Absolute energy is -572.6949094 E$_h$.

Table S3. Rotational parameters predicted at B3LYP-D3/6-311++G(d,p) level of theory for the stable conformers of the dihydrated complex of the salicylic acid.

Parameter[a]	I-2wa	II-2wa	I-2wab	III-2wa
A/MHz	1780.40	1759.99	1164.04	1385.97
B/MHz	453.67	450.32	526.32	613.62
C/MHz	362.04	359.17	362.96	504.06
P_{cc}/u$\mathrm{\AA}^2$	0.96	1.17	0.99	92.81
μ_a/D	-0.5	0.8	-2.6	-1.4
μ_b/D	-0.9	-0.8	0.2	1.2
μ_c/D	0.0	0.0	2.2	-1.1
ΔE_{DFT}/cm^{-1}	0.0 [b]	693.9	2401.6	3571.7

[a] See footnote of Table S1.

[b] Absolute energy is -649.1747737 E_h.

Table S4. Rotational parameters predicted at B3LYP-D3/6-311++G(d,p) level of theory for the stable conformers of the trihydrated complex of the salicylic acid.

Parameter[a]	I-w₃-a	I-w₃-b	I-w₃-c
A/MHz	1412.10	1436.05	1421.44
B/MHz	319.03	317.16	327.39
C/MHz	263.04	262.98	284.18
P_{cc}/uÅ^2	10.33	11.82	60.41
μ_a/D	0.6	-0.1	-1.5
μ_b/D	0.6	0.0	1.3
μ_c/D	0.6	0.3	-0.1
ΔE_{DFT}/cm^{-1}	0.0 [b]	130.4	130.4
	I-w₃-d	**II-w₃-a**	**I-w₃-e**
A/MHz	1299.61	1352.11	1155.81
B/MHz	372.95	320.69	379.40
C/MHz	335.34	261.57	318.21
P_{cc}/uÅ^2	118.44	8.79	90.55
μ_a/D	1.1	0.9	-0.1
μ_b/D	-1.4	1.2	3.0
μ_c/D	1.2	0.8	1.0
ΔE_{DFT}/cm^{-1}	378.2	575.6	846.4

[a] See footnote of Table S1.

[b] Absolute energy is -725.6502119 E_h.

Table S5. Rotational parameters predicted at B3LYP-D3/6-311++G(d,p) level of theory for the stable conformers of the tetrahydrated complex of the salicylic acid.

Parameter[a]	I-w$_4$-a	I-w$_4$-b	I-w$_4$-c
A/MHz	1073.10	1066.29	1059.87
B/MHz	250.60	251.56	251.90
C/MHz	222.98	224.02	224.40
P_{cc}/uÅ^2	110.58	113.49	115.48
μ_a/D	-0.8	-0.7	0.8
μ_b/D	1.4	1.6	1.3
μ_c/D	0.2	0.4	1.6
ΔE_{DFT}/cm^{-1}	0.0 [b]	165.7	241.2
	I-w$_4$-d	**I-w$_4$-e**	**I-w$_4$-f**
A/MHz	1093.11	1028.22	1137.26
B/MHz	243.76	289.50	276.83
C/MHz	217.21	261.57	244.94
P_{cc}/uÅ^2	104.46	152.55	130.35
μ_a/D	0.6	-1.4	-1.3
μ_b/D	-3.1	0.1	-1.5
μ_c/D	0.5	0.5	0.1
ΔE_{DFT}/cm^{-1}	267.8	269.6	336.5
	I-w$_4$-g	**II-w$_4$-a**	**I-w$_4$-h**
A/MHz	1045.06	1062.27	1053.34
B/MHz	251.42	251.68	288.32
C/MHz	227.64	222.95	260.13
P_{cc}/uÅ^2	136.80	112.50	144.92
μ_a/D	0.4	1.1	-0.1
μ_b/D	-3.1	3.0	1.6
μ_c/D	0.3	-0.2	2.7
ΔE_{DFT}/cm^{-1}	509.7	535.3	591.6

[a] See footnote of Table S1.

[b] Absolute energy is -802.1296231 E$_h$.

Table S6. Experimental rotational parameters obtained for the observed ^{13}C and D isotopologues of conformer I of salicylic acid. The D species were also fit with the transitions of the millimetre-wave previous study [11]. The centrifugal distortion constants for all the isotopologues were fixed to the parent values. See Figure 3 or Table S9 for the atom labelling.

Fitted Param.[a]	$^{13}C_1$	$^{13}C_2$	$^{13}C_3$	$^{13}C_4$	$^{13}C_5$
A/MHz	2339.6062(13)[b]	2330.4567(20)	2330.9608(16)	2339.51690(98)	2317.03428(97)
B/MHz	1223.74657(95)	1222.93965(80)	1212.7043(10)	1203.85694(74)	1212.8771(11)
C/MHz	803.81184(76)	802.37992(76)	798.02404(70)	795.17425(46)	796.45755(66)
P_{cc}/uÅ^2	0.12957(52)	0.12884(53)	0.13036(52)	0.13043(36)	0.12946(50)
N	11	7	10	10	13
σ/kHz	9.5	7.4	8.6	5.5	8.1

	$^{13}C_6$	$^{13}C_{11}$
A/MHz	2317.03232(94)	2339.7700(13)
B/MHz	1222.93849(56)	1215.9562(12)
C/MHz	800.78462(60)	800.46268(82)
P_{cc}/uÅ^2	0.12987(38)	0.12963(59)
N	13	10
σ/kHz	6.9	8.4

	D_{15}	D_{16}	D_{15} -D_{16}
A/MHz	2323.77041(21)	2297.80023(28)	2280.69331(29)
B/MHz	1194.46860(18)	1220.49531(35)	1191.70809(50)
C/MHz	798.26545(21)	797.43514(34)	783.04691(44)
P_{cc}/uÅ^2	0.13307(13)	0.13085(21)	0.13446(28)
N	53[c]	52[c]	43[c]
σ/kHz	15.4	21.5	19.4

[a] A, B and C are the rotational constants. P_{cc} is the planar moment of inertia, derived from $P_{cc}=(I_a+I_b-I_c)/2$. Δ_J, Δ_{JK}, Δ_K, δ_J and δ_K are the quartic centrifugal distortion constants. N is the number of rotational transitions fitted. σ is the rms deviations of the fit.
[b] Standard error is given in parentheses in units of the last digit.
[c] Fit done with the transition measured in the previous work [11].

Table S7. Experimental rotational parameters obtained for the observed D isotopologues of conformer SA-w (I-w-a) of salicylic acid – water cluster. The centrifugal distortion constants for all the isotopologues were fixed to the parent values. See Figure S3 or Table S12 for the atom labelling.

Fitted Param.[a]	D_{15}	D_{16}	D_{18}	D_{19}
A/MHz	2303.2538(24)[b]	2270.4682(19)	2311.152(15)	2311.8536(35)
B/MHz	638.94582(43)	644.94882(32)	634.33584(77)	625.31918(61)
C/MHz	500.70308(30)	502.79168(22)	498.25634(52)	492.99050(33)
P_{cc}/uÅ²	0.51920(68)	0.51881(51)	0.5401(17)	0.83388(90)
N	14	13	10	11
σ/kHz	7.2	5.5	7.7	8.9

[a] A, B and C are the rotational constants. P_{cc} is the planar moment of inertia, derived from $P_{cc}=(I_a+I_b-I_c)/2$. N is the number of rotational transitions fitted. σ is the rms deviations of the fit.

[b] Standard error is given in parentheses in units of the last digits.

Table S8. r_s and r_m geometry parameters (lengths in Å and angles in degree) experimentally determined and their comparison with the r_e structure predicted at B3LYP-D3/6-311++G(d,p) level of theory and with the r_a structure obtained by gas-phase electron diffraction [12] for the conformer I of salicylic acid. For the r_m structure the $r_m^{(1L)}$ definition has been chosen. This definition employs C_α coefficients to reproduce the vibration-rotation term in order to obtain the mass-dependant moments of inertia from the effective ones. The different C_α constants were estimated to have similar values so in the final fits these were assumed to be equal. The L refers to the parameter δ_H for all r_m-r(C-H) bonds, which in this case was fixed to 0.01 Å [60]. See Figure 3 or Table S9 for atom labelling.

Parameter	r_s	$r_m^{(1L)}$	r_a [a]	r_e
r(C$_1$-C$_2$)	–	1.4091(51)	1.419(3)	1.417
r(C$_2$-C$_3$)	1.4114(31)[b]	1.4064(67)	1.407(6)	1.402
r(C$_3$-C$_4$)	1.3813(51)	1.3809(96)	1.395(4)	1.384
r(C$_4$-C$_5$)	1.4083(50)	1.4120(87)	1.413(6)	1.402
r(C$_5$-C$_6$)	1.3920(30)	1.3841(73)	1.396(4)	1.383
r(C$_1$-C$_6$)	-	1.4031(79) [c]	1.410(6)	1.408
r(C$_1$-C$_{11}$)	-	1.4682(83)	1.465(8)	1.465
r(C$_2$-O$_{12}$)	-	1.342(13)	1.333(7)	1.344
r(C$_{11}$-O$_{13}$)	-	1.3496(42) [c]	1.339(7)	1.350
r(C$_{11}$-O$_{14}$)	-	1.2258(42) [c]	1.228(6)	1.226
r(O$_{12}$-H$_{16}$)	-	0.990(14)	1.051(20)	0.980
r(O$_{13}$-H$_{15}$)	-	0.9685(19) [c]	1.063(20)	0.968
r(O$_{14}\cdots$H$_{16}$)	-	1.7569(40) [c]	1.727(14)	1.775
∠(C$_1$-C$_2$-C$_3$)	-	119.2(5) [c]	120.0(3)	119.2
∠(C$_2$-C$_3$-C$_4$)	120.1(2)	120.1(3)	120.8(3)	120.2
∠(C$_3$-C$_4$-C$_5$)	120.8(1)	120.9(1)	118.5(3)	121.0
∠(C$_4$-C$_5$-C$_6$)	119.2(1)	119.1(3)	122.0(3)	119.3
∠(C$_1$-C$_6$-C$_5$)	-	120.7(5) [c]	119.1(3)	120.9
∠(C$_2$-C$_1$-C$_6$)	-	119.9(7) [c]	119.6(3)	119.3
∠(C$_2$-C$_1$-C$_{11}$)	-	118.4(5) [c]	-	119.0
∠(C$_6$-C$_1$-C$_{11}$)	-	121.7(5) [c]	-	121.7
∠(C$_1$-C$_2$-O$_{12}$)	-	123.5(8) [c]	-	123.3
∠(C$_3$-C$_2$-O$_{12}$)		117.2(6)	-	117.5
∠(C$_1$-C$_{11}$-O$_{13}$)	-	113.9(3)	-	114.7
∠(C$_1$-C$_{11}$-O$_{14}$)	-	125.3(4) [c]	-	124.5
∠(C$_2$-O$_{12}$-H$_{16}$)	-	107.6(6)	-	108.2
∠(C$_{11}$-O$_{13}$-H$_{15}$)	-	105.4(2)	-	107.1
∠(O$_{12}$-H$_{16}$-O$_{14}$)	-	145.4(3) [c]	-	144.5
C_α[d] / u$^{1/2}\cdot$Å	-	0.01742(35)	-	-
δ_H / u$^{1/2}\cdot$Å	-	[0.010][e]	-	-
σ_{fit}[f] / u$\cdot$Å^2	-	0.009792	-	-

[a] The r_a structure has been taken from the reference 12. [b] Standard error is given in parenthesis in units of the last digit. [c] Derived parameters. [d] Fitted using the assumption $C_\alpha = C_a = C_b = C_c$. [e] Fixed values for H$_{15}$ and H$_{16}$. [f] Standard deviation of the fit of all the rotational constants.

Table S9. Principal inertial axis coordinates for the atoms of conformer I of salicylic acid. The table compares the theoretical coordinates (r_e) calculated at the B3LYP-D3/6-311++G(d,p) level of theory with the experimental r_s and r_m coordinates. The definition $r_m^{(1L)}$ was chosen for the r_m determination. [60]. The hydrogen H_{15} and H_{16} coordinates were also compared with the obtained r_s coordinates in the previous study [11].

atom	method	a	b	c
C_1	r_e	0.1737	0.2305	0.000
	r_m	0.1675(82)[a]	0.2623(59)	0.000
	r_s	[0.000][b]	0.2446(34)	0.000
C_2	r_e	-0.5442	-0.9618	0.000
	r_m	-0.5362(63)	-0.9585(42)	0.000
	r_s	-0.5292(30)	-0.9552(16)	0.000
C_3	r_e	-1.9455	-0.9330	0.000
	r_m	-1.9425(20)	-0.9411(48)	0.000
	r_s	-1.94056(78)	-0.9384(16)	0.000
C_4	r_e	-2.6183	0.2770	0.000
	r_m	-2.6201(14)	0.2622(89)	0.000
	r_s	-2.61820(58)	0.2652(57)	0.000
C_5	r_e	-1.9182	1.4923	0.000
	r_m	-1.9210(21)	1.4890(29)	0.000
	r_s	-1.91901(78)	1.4877(10)	0.000
C_6	r_e	-0.5356	1.4766	0.000
	r_m	-0.5370(70)	1.4758(30)	0.000
	r_s	-0.5271(29)	1.4749(10)	0.000
H_7	r_e	-2.4743	-1.8779	0.000
	r_m	-2.4635(49)	-1.8904(64)	0.000
	r_s	-	-	-
H_8	r_e	-3.7027	0.2806	0.000
	r_m	-3.7046(14)	0.260(13)	0.000
	r_s	-	-	-
H_9	r_e	-2.4542	2.4332	0.000
	r_m	-2.4614(41)	2.4274(32)	0.000
	r_s	-	-	-
H_{10}	r_e	0.0249	2.4023	0.000
	r_m	0.0218(66)	2.4025(41)	0.000
	r_s	-	-	-
C_{11}	r_e	1.6381	0.2238	0.000
	r_m	1.6351(14)	0.2225(36)	0.000
	r_s	1.63196(93)	0.2128(71)	0.000
O_{12}	r_e	0.0514	-2.1663	0.000
	r_m	0.063(14)	-2.1592(40)	0.000
	r_s	-	-	-

[a] Standard error is given in parentheses in units of the last digits.

[b] r_s parameters in square brackets are fixed to zero owing to the Kraitchman equations give imaginary values.

Table S9 (Continued).

atom	method	a	b	c
O₁₃	r_e	2.2323	1.4356	0.000
	r_m	2.2153(15)[a]	1.4411(28)	0.000
	r_s	-	-	-
O₁₄	r_e	2.3070	-0.8034	0.000
	r_m	2.3157(33)	-0.7969(26)	0.000
	r_s	-	-	-
H₁₅	r_e	3.1887	1.2831	0.000
	r_m	3.1689(11)	1.2722(28)	0.000
	r_s	3.17210(86)	1.2696(12)	0.000
	r_s [c]	3.173(1)	1.270(1)	0.000
H₁₆	r_e	1.0221	-2.0284	0.000
	r_m	1.0412(33)	-2.0068(17)	0.000
	r_s	1.0414(11)	-2.0064(17)	0.000
	r_s [c]	1.045(5)	-2.004(1)	0.000

[a] Standard error is given in parentheses in units of the last digit.

[c] r_s coordinates taken from reference 11.
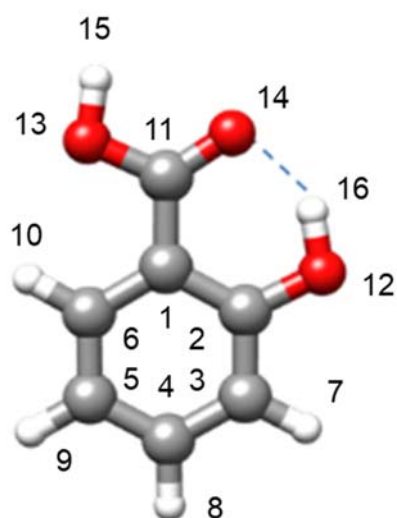
Table S10. Predicted stabilizing delocalization energies from the NBO calculations done at B3LYP-D3/6-311++G(d,p) level of theory for the observed I, I-w-a, I-w$_2$-a, I-w$_3$-a and I-w$_4$-a species of salicylic acid and its hydrates. The delocalization energies in the first case are the donor-acceptor conjugative stabilization energies which informs about the charge transfer between $\pi \leftarrow \pi^*$ orbitals. In the second case they are the electron delocalization energies from the lone pair n_0 of the oxygen atoms to the σ^* orbital of the hydrogen atoms, which characterize the hydrogen bonds.

π	π^*	E / kcal·mol^{-1}				
		I	I-w-a	I-w$_2$-a	I-w$_3$-a	I-w$_4$-a
C_1-C_2	C_3-C_4	13.32	13.45	13.52	14.20	14.21
	C_5-C_6	22.88	22.87	22.85	24.01	23.92
	C_{11}-O_{14}	29.66	30.88	31.20	31.07	32.13
C_3-C_4	C_1-C_2	24.44	24.31	24.27	26.02	26.04
	C_5-C_6	15.55	15.47	15.47	15.55	15.49
C_5-C_6	C_1-C_2	15.00	15.00	14.01	16.12	16.15
	C_3-C_4	22.61	22.77	22.82	22.93	23.04
C_{11}-O_{14}	C_1-C_2	2.84	2.67	2.55	3.20	3.11
n_0	σ^*					
O_{12}	C_1-C_2	37.21	36.93	36.64	41.99	41.79
O_{13}	C_{11}-O_{14}	45.23	53.96	59.03	62.85	68.7
O_{14}	C_1-C_{11}	13.13	12.43	12.89	13.42	13.93
	C_{11}-O_{13}	30.40	26.45	24.86	25.32	23.47
	O_{12}-H_{16}	16.02	17.15	17.21	18.32	18.11
O_{17}	O_{13}-H_{15}	-	17.59	29.75	30.46	42.55
O_{14}	O_{17}-H_{18}	-	3.08	-	-	-
	O_{20}-H_{21}	-	-	4.39	2.73	8.41
O_{20}	O_{17}-H_{18}	-	-	16.96	-	0.19
	O_{23}-H_{24}	-	-	-	21.33	-
	O_{26}-H_{27}	-	-	-	-	12.89
O_{23}	O_{17}-H_{18}	-	-	-	18.25	-
	O_{17}-H_{19}	-	-	-	-	16.19
O_{26}	O_{23}-H_{24}	-	-	-	-	15.04
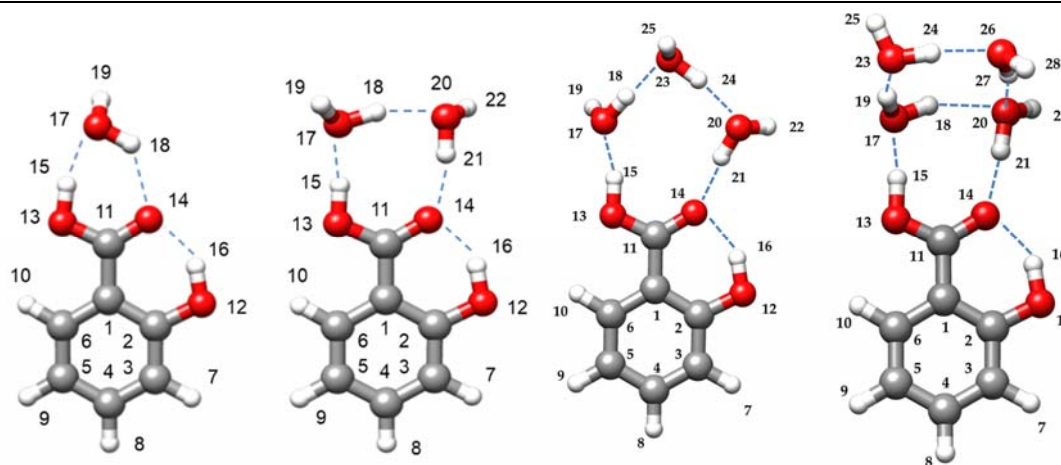
Table S11. Predicted bond orders from the NBO calculations done at B3LYP-D3/6-311++G(d,p) level of theory for the observed I, I-w-a, I-w$_2$-a, I-w$_3$-a and I-w$_4$-a species of salicylic acid and its hydrates.

		I	I-w-a	I-w$_2$-a	I-w$_3$-a	I-w$_4$-a
C$_1$	C$_2$	1.3789	1.3869	1.3882	1.3209	1.3361
	C$_6$	1.4011	1.4034	1.3991	1.4120	1.4261
	C$_{11}$	1.0299	1.0287	1.0266	1.0313	1.0369
C$_2$	C$_3$	1.3993	1.4044	1.4025	1.4051	1.3906
	O$_{12}$	1.0941	1.0931	1.0917	1.1207	1.1283
C$_3$	C$_4$	1.4869	1.4958	1.4859	1.5712	1.5537
C$_4$	C$_5$	1.4355	1.4379	1.4426	1.4301	1.4370
C$_5$	C$_6$	1.4922	1.5036	1.5002	1.5431	1.5400
C$_{11}$	O$_{13}$	1.2120	1.3003	1.3314	1.1943	1.3029
	O$_{14}$	1.7204	1.6592	1.6285	1.5783	1.4917
O$_{12}$	H$_{16}$	0.9728	0.9720	0.9719	0.8902	0.8978
O$_{13}$	H$_{15}$	0.9886	0.9699	0.9580	0.8283	0.7508
O$_{17}$	H$_{18}$	-	1.0000	0.9802	0.8637	0.9544
	H$_{19}$	-	0.9919	1.0000	1.0000	0.8949
O$_{20}$	H$_{21}$	-	-	0.9854	0.9364	0.9176
	H$_{22}$	-	-	1.0000	1.0000	1.0000
O$_{23}$	H$_{24}$	-	-	-	0.8852	0.9039
	H$_{25}$	-	-	-	1.0000	1.0000
O$_{26}$	H$_{27}$	-	-	-	-	0.9186
	H$_{28}$	-	-	-	-	1.0000
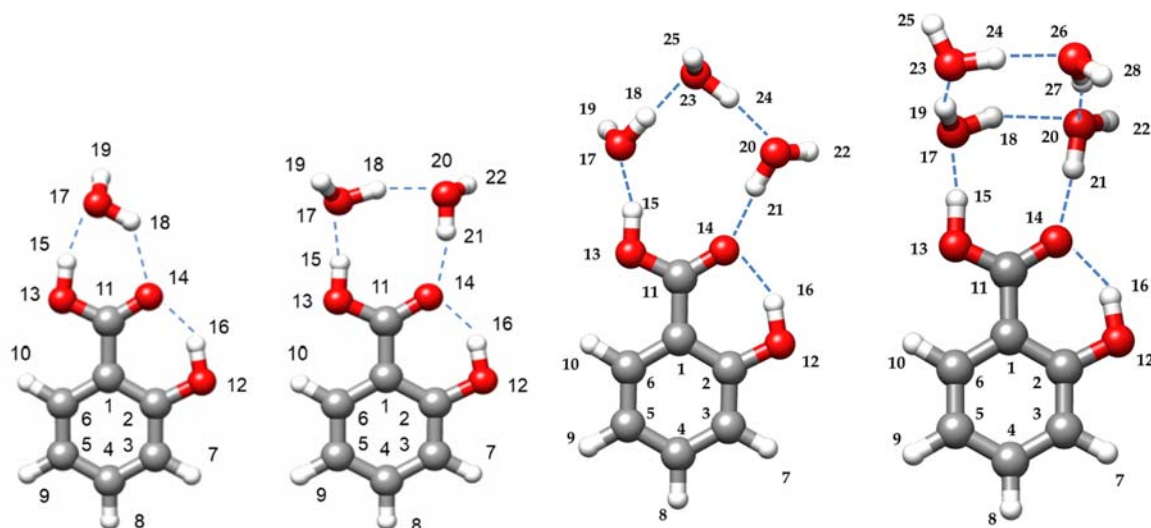
Table S12. r_s, and r_0 geometry parameters (lengths in Å and angles in degree) experimentally determined and their comparison with the r_e structure predicted at B3LYP-D3/6-311++G(d,p) level of theory for the conformer I-w-a of salicylic acid monohydrated cluster.

Parameter	r_s	r_0	r_e
$r(H_{15}\text{-}H_{18})$	1.9287(44)[a]	1.9223(54)[b]	1.993
$r(C_{11}\text{-}O_{13})$	-	1.3496(10)[b]	1.330
$r(C_{11}\text{-}O_{14})$	-	1.22576(98)[b]	1.239
$r(C_{12}\text{-}O_{16})$	-	1.0490(80)	0.981
$r(O_{13}\text{-}H_{15})$	-	1.0065(13)	0.988
$r(O_{17}\text{-}H_{18})$	-	0.9650(42)[b]	0.972
$r(O_{14}\cdots H_{16})$	-	1.7019(60)[b]	1.754
$r(H_{15}\cdots O_{17})$	-	1.7531(24)	1.764
$r(O_{14}\cdots H_{18})$	-	1.9819(25)	2.031
$\angle(C_{11}\text{-}O_{13}\text{-}H_{15})$	-	108.5(1)	108.9
$\angle(C_2\text{-}O_{12}\text{-}H_{16})$	-	107.0(1)	107.8
$\angle(O_{13}\text{-}H_{15}\cdots O_{17})$	-	160.6(2)	158.9
$\angle(C_{11}\text{-}O_{14}\cdots H_{18})$	-	109.2(2)	109.5
$\angle(O_{14}\cdots H_{18}\text{-}O_{17})$	-	136.7(4)[b]	132.1
$\angle(O_{13}\text{-}H_{15}\cdots O_{17}\text{-}H_{19})$	-	119.4(8)	117.9
$\angle(C_{11}\text{-}O_{13}\text{-}H_{15}\cdots O_{17})$		-13.8(5)	-4.5
$\angle(C_1\text{-}C_{11}\text{-}O_{14}\cdots H_{18})$		173.9(5)	179.8
σ_{fit}[c] / u · Å^2	-	0.005575	-

[a] Standard error is given in parenthesis in units of the last digit.

[b] Derived parameters.

[c] Standard deviation of the fit of all the rotational constants.
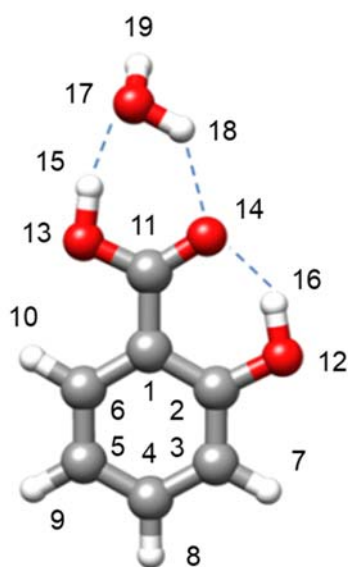
Table S13. Principal inertial axis coordinates for the selected atoms of conformer I-w-a of salicylic acid monohydrated cluster. The table compares the theoretical coordinates calculated at the B3LYP-D3/6-311++G(d,p) level of theory with the experimental r_s and r_0 coordinates.

atom	method	a	b	c
H$_{15}$	r_e	2.7275	1.1018	-0.0056
	r_s	2.73986(55)[a]	1.0767(14)	-0.046(33)
	r_0	2.7404(11)	1.0744(27)	-0.0406(16)
H$_{16}$	r_e	0.3529	-2.0915	0.0026
	r_s	0.3976(38)	-2.07723(73)	[0.000][b]
	r_0	0.4015(77)	-2.0761(14)	0.01323(39)
H$_{18}$	r_e	3.7000	-0.6373	0.0035
	r_s	3.63884(43)	-0.6182(26)	0.152(11)
	r_0	3.63926(90)	-0.6140(50)	0.151(19)
H$_{19}$	r_e	4.9103	0.1122	-0.6267
	r_s	4.94329(31)	0.117(13)	-0.5712(27)
	r_0	4.94376(64)	0.045(12)	-0.5742(46)

[a] Standard error is given in parentheses in units of the last digit.

[b] r_s parameters in square brackets are fixed to zero owing to the Kraitchman equations give imaginary values.
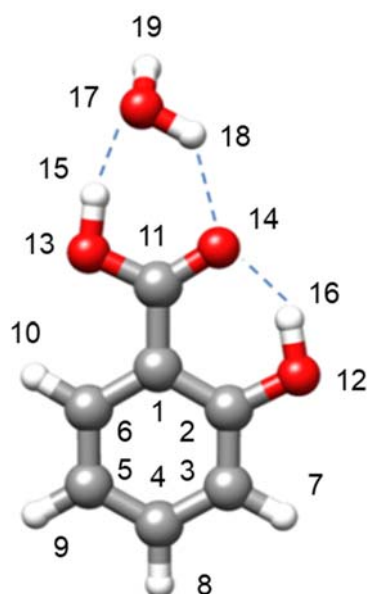
Table S14. r_e geometrical parameters (lengths in Å and angles in degree) predicted at B3LYP-D3/6-311++G(d,p) level of theory for the conformer I-w₂-a of salicylic acid dihydrated cluster.

Parameter	r_e
$r(O_{12}-H_{16})$	0.980
$r(O_{14}\cdots H_{16})$	1.749
$r(C_{11}-O_{13})$	1.317
$r(C_{11}-O_{14})$	1.243
$r(O_{13}-H_{15})$	1.002
$r(O_{17}-H_{18})$	0.984
$r(O_{20}-H_{21})$	0.979
$r(H_{15}\cdots O_{17})$	1.647
$r(O_{14}\cdots H_{21})$	1.806
$r(O_{20}\cdots H_{18})$	1.749
$\angle(O_{13}-H_{15}\cdots O_{17})$	176.3
$\angle(O_{14}\cdots H_{21}-O_{20})$	166.0
$\angle(O_{17}-H_{18}\cdots O_{20})$	157.7
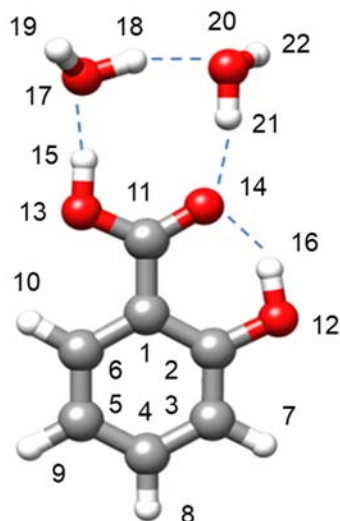
Table S15. r_e geometrical parameters (lengths in Å and angles in degree) predicted at B3LYP-D3/6-311++G(d,p) level of theory for the conformer I-w₃-a of salicylic acid trihydrated cluster.

Parameter	r_e
$r(O_{12}-H_{16})$	0.981
$r(O_{14}\cdots H_{16})$	1.748
$r(C_{11}-O_{13})$	1.314
$r(C_{11}-O_{14})$	1.243
$r(O_{13}-H_{15})$	1.004
$r(O_{17}-H_{18})$	0.988
$r(O_{20}-H_{21})$	0.978
$r(O_{23}-H_{24})$	0.984
$r(H_{15}\cdots O_{17})$	1.627
$r(O_{14}\cdots H_{21})$	1.787
$r(O_{20}\cdots H_{24})$	1.734
$r(O_{23}\cdots H_{18})$	1.707
$\angle(O_{13}-H_{15}\cdots O_{17})$	167.4
$\angle(O_{14}\cdots H_{21}-O_{20})$	175.7
$\angle(O_{17}-H_{18}\cdots O_{23})$	173.3
$\angle(O_{23}-H_{24}\cdots O_{20})$	165.6
$\angle(C_1-C_{11}-O_{13}-H_{15})$	-177.4
$\angle(C_1-C_{11}-O_{13}\cdots O_{17})$	-175.7
$\angle(C_1-C_{11}-O_{13}\cdots O_{23})$	170.5
$\angle(C_1-C_{11}-O_{14}\cdots O_{20})$	-153.7
$\angle(C_1-C_{11}-O_{14}\cdots O_{23})$	-169.1
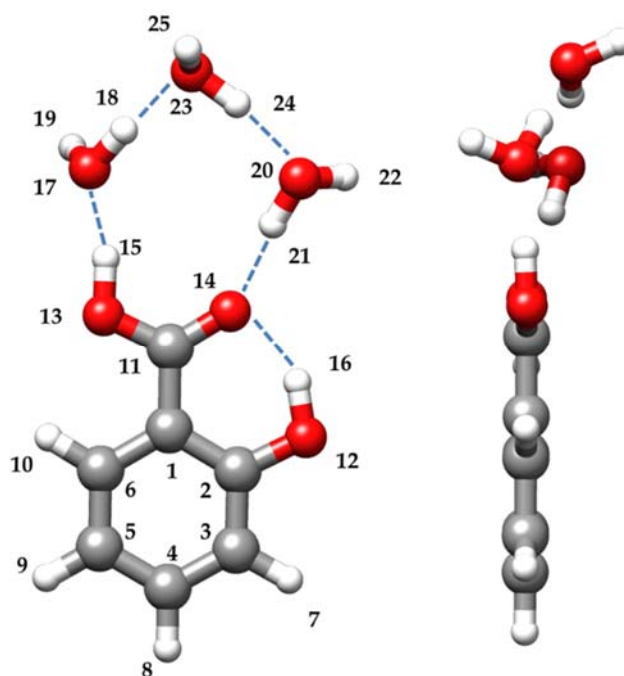
Table S16. r_e geometrical parameters (lengths in Å and angles in degree) predicted at B3LYP-D3/6-311++G(d,p) level of theory for the conformer I-w4-a of salicylic acid tetrahydrated cluster.

Parameter	r_e
r(O$_{12}$-H$_{16}$)	0.981
r(O$_{14}$···H$_{16}$)	1.742
r(C$_{11}$-O$_{13}$)	1.307
r(C$_{11}$-O$_{14}$)	1.250
r(O$_{13}$-H$_{15}$)	1.020
r(O$_{17}$-H$_{18}$)	0.970
r(O$_{17}$-H$_{19}$)	0.983
r(O$_{20}$-H$_{21}$)	0.987
r(O$_{23}$-H$_{24}$)	0.981
r(O$_{26}$-H$_{27}$)	0.978
r(H$_{15}$···O$_{17}$)	1.557
r(O$_{14}$···H$_{21}$)	1.710
r(O$_{20}$···H$_{18}$)	1.972
r(O$_{20}$···H$_{27}$)	1.817
r(O$_{23}$···H$_{19}$)	1.779
r(O$_{26}$···H$_{24}$)	1.789
∠(O$_{13}$-H$_{15}$···O$_{17}$)	175.9
∠(O$_{14}$···H$_{21}$-O$_{20}$)	174.7
∠(O$_{17}$-H$_{18}$···O$_{20}$)	146.9
∠(O$_{17}$-H$_{19}$···O$_{23}$)	165.1
∠(O$_{23}$-H$_{24}$···O$_{26}$)	164.8
∠(O$_{26}$-H$_{27}$···O$_{20}$)	167.9
∠(C$_1$-C$_{11}$-O$_{13}$···O$_{17}$)	179.6
∠(C$_1$-C$_{11}$-O$_{14}$···O$_{20}$)	179.0
∠(O$_{13}$···O$_{17}$···O$_{23}$)	114.6
∠(O$_{14}$···O$_{20}$···O$_{26}$)	110.8
∠(O$_{13}$···O$_{17}$···O$_{20}$···O$_{26}$)	-109.6
∠(O$_{13}$···O$_{17}$···O$_{20}$···O$_{26}$)	113.8
∠(C$_{11}$-O$_{13}$···O$_{17}$···O$_{23}$)	-92.6
∠(C$_{11}$-O$_{14}$···O$_{20}$···O$_{26}$)	87.4
∠(O$_{17}$···O$_{20}$···O$_{26}$···O$_{23}$)	-0.9
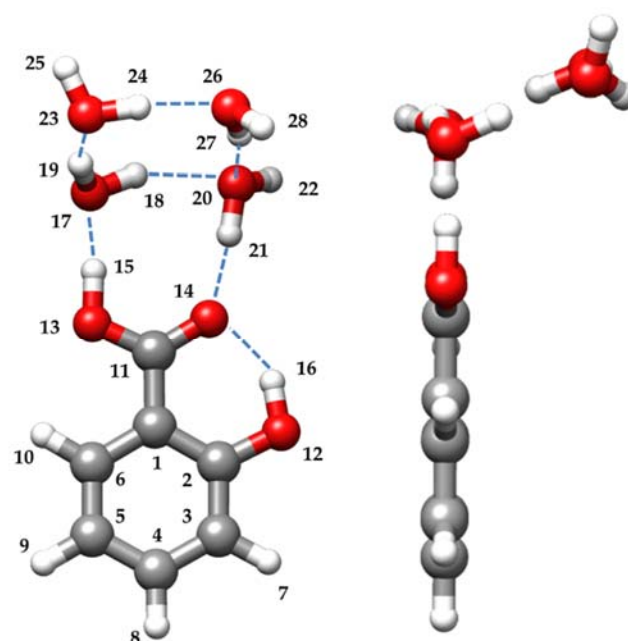
Table S17. Observed rotational transitions and residuals (all the values in MHz) for conformer I of the salicylic acid in the ground vibrational state. The lines with frequencies above 8 GHz were measured in the MB-FTMW spectrometer as a thermal recombination product in the spectroscopic analysis of *o*-anisic acid [36].

J′	K₋₁′	K₊₁′	J″	K₋₁″	K₊₁″	Obs.	Obs.-Cal.	J′	K₋₁′	K₊₁′	J″	K₋₁″	K₊₁″	Obs.	Obs.-Cal.
1	1	1	0	0	0	3144.1569	0.0084	1	1	1	0	0	0	3144.1569	0.0084
2	0	2	1	1	1	2840.9720	-0.0044	5	3	3	5	2	4	7352.2379	0.0009
2	1	2	1	0	1	4751.9445	0.0007	5	4	2	5	3	2	8795.5073	0.0002
2	2	1	1	1	0	7824.6411	-0.0060	5	4	3	5	3	3	9151.9816	0.0001
2	1	1	2	0	2	2054.0953	-0.0037	6	2	6	5	3	3	8441.1694	0.0001
2	2	0	2	1	1	3447.3062	-0.0122	6	2	5	5	3	2	4016.5305	-0.0099
2	2	1	2	1	2	4609.0603	0.0043	6	3	5	5	4	2	4236.6208	0.0013
3	1	3	2	1	2	5397.7466	-0.0146	6	2	3	6	1	5	4899.8952	-0.0094
3	2	1	2	2	0	6443.8813	0.0179	6	2	4	6	1	6	8672.1102	0.0001
3	0	3	2	1	2	4927.6352	-0.0115	6	3	6	6	2	4	4947.4359	0.0043
3	1	3	2	0	2	6192.2528	0.0055	6	4	5	6	3	3	8321.1307	-0.0003
3	1	2	2	2	1	3293.1922	-0.0033	6	4	4	6	3	4	9234.4157	0.0005
3	2	2	2	1	1	9432.4424	0.0014	7	2	5	6	3	3	4494.8206	0.0025
3	1	2	3	0	3	2974.6056	0.0007	7	3	6	6	4	3	7226.8784	0.0017
3	2	1	3	1	2	3248.5485	0.0052	7	3	5	6	4	2	5078.3827	-0.0022
3	2	2	3	1	3	5294.2991	0.0064	7	1	7	7	0	7	9690.3441	-0.0013
3	3	0	3	2	1	6243.5029	0.0014	7	2	3	7	1	6	6427.5530	0.0017
3	3	1	3	2	2	6687.5098	0.0020	7	3	1	7	2	5	4993.9969	0.0087
4	0	4	3	0	3	7344.3581	0.0050	7	3	2	7	2	6	8904.6994	0.0014
4	0	4	3	1	3	6874.2407	0.0021	7	4	4	7	3	4	7651.2910	0.0085
4	1	4	3	0	3	7581.6410	-0.0111	7	4	5	7	3	5	9456.0961	0.0010
4	1	3	3	2	2	5916.1901	-0.0027	8	2	3	8	1	7	8289.4650	0.0010
4	1	3	4	0	4	4336.2379	-0.0090	8	3	4	8	2	6	5576.9324	-0.0152
4	2	2	4	1	3	3340.5304	-0.0006	8	4	5	8	3	5	6963.7282	0.0040
4	2	3	4	1	4	6216.2529	-0.0077	8	4	3	8	3	6	9873.7942	0.0011
4	3	1	4	2	2	5800.5691	-0.0151	9	3	2	9	2	7	6752.9531	-0.0135
4	3	2	4	2	3	6924.0407	-0.0047	9	4	3	9	3	6	6524.7030	-0.0159
4	4	1	4	3	2	9147.2357	-0.0015	10	3	6	10	2	8	8454.1179	0.0003
5	0	5	4	1	4	8675.8944	0.0004	10	5	4	10	4	6	9351.3204	-0.0003
5	1	5	4	0	4	9020.2548	0.0005	5	3	5	5	2	4	7352.2379	0.0009
5	1	4	4	2	3	8491.9491	-0.0002								
5	2	3	4	3	2	5431.8666	0.0022								
5	1	4	5	0	5	6032.3278	0.0116								
5	2	3	5	1	4	3863.9545	-0.0058								
5	2	4	5	1	5	7355.1534	-0.0039								
5	3	2	5	2	3	5290.7705	-0.0007								

Table S18. Observed rotational transitions and residuals (all the values in MHz) for the ^{13}C isotopomers of conformer I of salicylic acid in the ground vibrational state.

$^{13}C_1$

J'	K-1'	K+1'	J''	K-1''	K+1''	Obs.	Obs.-Cal.
2	1	2	1	0	1	4751.0232	-0.0181
3	1	3	2	0	2	6191.1651	-0.0094
3	3	0	3	2	1	6240.3156	0.0098
4	0	4	3	1	3	6873.9352	0.0062
4	1	4	3	0	3	7580.4789	0.0016
4	1	3	3	2	2	5917.5879	0.0081
4	1	3	4	0	4	4336.4057	0.0054
4	2	3	4	1	4	6214.8713	-0.0136
4	3	1	4	2	2	5797.2780	0.0111
5	3	2	5	2	3	5287.5748	-0.0043
6	3	3	6	2	4	4944.7776	-0.0003

$^{13}C_2$

J'	K-1'	K+1'	J''	K-1''	K+1''	Obs.	Obs.-Cal.
2	1	2	1	0	1	4737.6000	0.0039
3	0	3	2	1	2	4926.2982	-0.0030
3	1	3	2	0	2	6174.9609	0.0000
4	0	4	3	1	3	6867.0631	0.0116
4	1	3	3	2	2	5932.5785	-0.0113
4	3	2	4	2	3	6883.4627	-0.0077
5	1	4	5	0	5	6033.8355	0.0061

$^{13}C_3$

J'	K-1'	K+1'	J''	K-1''	K+1''	Obs.	Obs.-Cal.
2	1	2	1	0	1	4725.0354	0.0028
3	0	3	2	1	2	4880.0778	-0.0088
3	1	3	2	0	2	6155.1422	0.0087
3	2	2	3	1	3	5274.9843	-0.0171
4	0	4	3	1	3	6815.5527	-0.0042
4	1	4	3	0	3	7533.4870	0.0028
4	1	3	4	0	4	4292.5050	-0.0042
4	2	3	4	1	4	6185.0092	-0.0004
4	3	2	4	2	3	6913.4251	-0.0023
5	2	4	5	1	5	7309.8770	0.0150

$^{13}C_4$

J'	K-1'	K+1'	J''	K-1''	K+1''	Obs.	Obs.-Cal.
2	1	2	1	0	1	4725.0354	-0.0038
2	1	1	2	0	2	2044.9233	-0.0071
3	0	3	2	1	2	4837.5965	-0.0072
3	1	3	2	0	2	6150.7572	0.0072
4	0	4	3	1	3	6772.7007	0.0054
4	1	4	3	0	3	7522.3372	-0.0035
4	1	3	4	0	4	4251.8141	0.0036
4	2	3	4	1	4	6193.9011	-0.0048
4	3	2	4	2	3	6975.2528	-0.0033
5	3	3	5	2	4	7380.7390	0.0068

$^{13}C_5$

J'	K-1'	K+1'	J''	K-1''	K+1''	Obs.	Obs.-Cal.
2	2	1	1	1	0	7747.5599	0.0024
3	0	3	2	1	2	4884.3544	-0.0095
3	1	3	2	0	2	6133.3180	0.0039
3	2	1	3	1	2	3213.5115	-0.0041
3	2	2	3	1	3	5241.4663	0.0190
3	3	0	3	2	1	6175.7001	-0.0021
3	3	1	3	2	2	6616.9130	-0.0046
4	0	4	3	1	3	6812.3164	0.0038
4	1	4	3	0	3	7510.0423	-0.0008
4	2	3	4	1	4	6155.9342	-0.0149
4	3	2	4	2	3	6851.9933	0.0056
5	2	3	5	1	4	3827.6305	0.0070
5	3	3	5	2	4	7277.4019	-0.0044

$^{13}C_6$

J'	K-1'	K+1'	J''	K-1''	K+1''	Obs.	Obs.-Cal.
1	1	1	0	0	0	3117.8024	-0.0144
2	1	2	1	0	1	4719.3813	-0.0044
2	2	1	1	1	0	7751.8921	0.0134
3	0	3	2	1	2	4929.4646	0.0081
3	1	3	2	0	2	6153.5491	0.0033
3	2	1	3	1	2	3191.0841	-0.0058
4	0	4	3	1	3	6862.7556	-0.0040
4	1	3	4	0	4	4341.8484	0.0007
4	2	2	4	1	3	3298.0640	0.0045
4	3	1	4	2	2	5681.1387	-0.0058
4	3	2	4	2	3	6824.8598	-0.0011
5	2	3	4	3	2	5546.8172	-0.0044
5	3	3	5	2	4	7262.2342	-0.0008

$^{13}C_{11}$

| J'	K-1'	K+1'	J''	K-1''	K+1''	Obs.	Obs.-Cal.
2	1	2	1	0	1	4741.1617	0.0041
2	2	1	1	1	0	7819.7501	-0.0196
3	0	3	2	1	2	4892.5132	0.0069
3	1	3	2	0	2	6175.7001	0.0015
3	2	1	3	1	2	3264.9584	0.0017
4	0	4	3	1	3	6834.5550	0.0014
4	2	3	4	1	4	6206.9918	0.0016
4	3	2	4	2	3	6943.1865	-0.0005
5	2	4	5	1	5	7334.0486	-0.0055
5	3	3	5	2	4	7362.4729	0.0149

Table S19. Observed rotational transitions and residuals (all the values in MHz) for the D isotopomer of conformer I of salicylic acid in the ground vibrational state.

D15

J′	K$_{-1}$′	K$_{+1}$′	J″	K$_{-1}$″	K$_{+1}$″	Obs.	Obs.-Cal.
3	0	3	2	1	2	4799.1786	-0.0144
3	1	3	2	0	2	6106.7554	-0.0029
3	2	1	3	1	2	3272.8064	0.0158
3	2	2	3	1	3	5262.9475	-0.0111
4	0	4	3	1	3	6720.5355	0.0053
4	1	4	3	0	3	7467.9881	0.0000
4	1	3	3	2	2	5675.3085	0.0099
4	1	3	4	0	4	4217.7278	0.0006
4	3	2	4	2	3	6931.8336	-0.0065
4	2	3	4	1	4	6150.8743	0.0004
4	3	1	4	2	2	5872.8458	-0.0062
5	1	4	5	0	5	5860.8630	0.0000
5	2	3	5	1	4	3806.4400	0.0064
6	1	5	6	0	6	7659.3144	0.0024
6	2	4	6	1	5	4766.3271	-0.0011
6	3	3	6	2	4	5000.6281	0.0026
7	3	4	6	4	3	6716.5451	0.0000
7	2	5	7	1	6	6210.2823	0.0003
7	3	4	7	2	5	4985.7092	0.0020
7	4	3	7	3	4	7792.6605	0.0051
8	4	5	7	5	2	4665.9047	-0.0011
8	3	5	8	2	6	5473.3292	-0.0036
8	4	4	8	3	5	7103.0519	0.0076
9	3	6	9	2	7	6531.3548	0.0018
9	4	5	9	3	6	6611.2054	-0.0083
10	4	6	10	3	7	6552.8229	-0.0005
11	4	7	11	3	8	7080.7922	-0.0009

D16

J′	K$_{-1}$′	K$_{+1}$′	J″	K$_{-1}$″	K$_{+1}$″	Obs.	Obs.-Cal.
4	1	1	2	0	2	2025.5524	-0.0010
4	0	3	2	1	2	4922.8451	-0.0155
2	1	3	2	0	2	6117.9076	0.0058
3	1	2	3	0	3	2961.0767	0.0130
3	2	1	3	1	2	3147.6445	0.0035
3	2	2	3	1	3	5193.3566	0.0009
3	3	0	3	2	1	6041.1232	0.0046
3	3	1	3	2	2	6501.8394	-0.0020
3	0	4	3	1	3	6844.1195	0.0083
3	1	4	3	0	3	7499.0788	0.0007
4	1	3	3	2	2	5989.8802	-0.0017
4	1	3	4	0	4	4339.1256	-0.0007
4	2	3	4	1	4	6124.0846	0.0115
4	3	1	4	2	2	5591.8242	0.0077
4	3	2	4	2	3	6747.6209	0.0071
4	1	4	5	0	5	6040.6141	0.0014
4	2	3	5	1	4	3825.6747	-0.0118
5	2	4	5	1	5	7271.3925	0.0044
5	2	4	6	1	5	4906.7594	-0.0086
5	3	3	6	2	4	4782.5530	-0.0005
6	3	4	6	2	5	7866.5361	0.0035
6	2	5	7	1	6	6471.9922	-0.0019
6	3	4	7	2	5	4887.8558	0.0000
7	3	5	8	2	6	5546.7901	0.0046
7	4	4	8	3	5	6671.7283	-0.0069
8	3	6	9	2	7	6802.2215	0.0030
8	4	5	9	3	6	6299.5059	-0.0133
9	4	6	10	3	7	6447.4680	-0.0084
9	4	7	11	3	8	7242.1196	-0.0066
10	5	7	12	4	8	7746.9645	-0.0022

D15-D16

J′	K$_{-1}$′	K$_{+1}$′	J″	K$_{-1}$″	K$_{+1}$″	Obs.	Obs.-Cal.
3	1	3	2	0	2	6032.8116	-0.0159
3	2	2	3	1	3	5159.8023	0.0082
4	0	4	3	1	3	6694.6938	0.0088
4	1	4	3	0	3	7386.0638	0.0030
4	1	3	4	0	4	4221.9313	-0.0046
5	1	4	5	0	5	5873.0339	-0.0080
5	2	3	5	1	4	3764.1728	0.0067
5	2	4	5	1	5	7165.5617	0.0043
6	1	5	6	0	6	7662.0479	0.0130
6	2	4	6	1	5	4770.6545	0.0000
6	3	3	6	2	4	4825.3072	0.0053
7	2	5	7	1	6	6256.1982	-0.0038
7	3	4	7	2	5	4867.8606	-0.0004
8	3	5	8	2	6	5431.8520	0.0091
9	3	6	9	2	7	6573.0172	-0.0102
9	4	5	9	3	6	6364.2018	-0.0093
10	4	6	10	3	7	6404.5960	-0.0034
11	4	7	11	3	8	7054.7648	-0.0025

Table S20. Observed rotational transitions and residuals (all the values in MHz) for the conformer I-w-a of the salicylic acid – water complex in the ground vibrational state. The lines with frequencies above 8 GHz were measured in the MB-FTMW spectrometer as a thermal recombination product in the spectroscopic analysis of *o*-anisic acid [36].

J′	K-1′	K+1′	J′′	K-1′′	K+1′′	Obs.	Obs.-Cal.	J′	K-1′	K+1′	J′′	K-1′′	K+1′′	Obs.	Obs.-Cal.
1	1	1	0	0	0	2820.3825	-0.0004	5	1	4	5	1	5	6300.6709	0.0085
2	1	1	1	1	0	2440.2790	-0.0016	5	1	3	5	1	4	4493.7493	0.0048
2	0	2	1	0	1	2291.7953	-0.0019	6	2	6	5	1	5	6421.4530	0.0057
2	1	2	1	0	1	3830.4594	-0.0001	6	2	6	5	0	5	6634.0042	-0.0064
2	2	0	1	1	1	7599.5574	0.0041	6	1	5	5	1	4	7244.1329	-0.0002
2	2	0	2	1	1	5019.2293	-0.0009	6	0	4	5	2	3	7129.1423	0.0026
2	2	1	2	1	2	5430.9205	0.0052	6	1	5	5	2	4	6862.8118	0.0059
3	0	3	2	0	2	3416.7925	-0.0001	6	2	3	5	3	2	6956.2422	0.0045
3	1	3	2	1	2	3235.1704	0.0027	6	2	4	5	3	3	6938.6901	0.0088
3	1	2	2	1	1	3654.9774	0.0025	6	3	2	5	4	1	6929.6329	0.0065
3	2	1	2	2	0	3483.9167	-0.0023	6	3	6	5	1	5	5713.9422	-0.0053
3	2	2	2	2	1	3450.3533	-0.0010	6	4	6	5	0	5	7341.5124	0.0020
3	1	3	2	0	2	4773.8281	-0.0019	6	0	5	6	0	6	3621.9393	-0.0007
3	2	2	2	1	1	8461.1408	-0.0021	6	1	4	6	1	5	4378.7504	-0.0005
3	1	2	3	0	3	2196.9807	0.0094	6	1	5	6	1	6	6742.0017	-0.0193
3	2	1	3	1	2	4848.1764	0.0020	7	2	7	6	1	6	7468.3652	-0.0045
3	2	2	3	1	3	5646.0997	-0.0021	7	2	7	6	0	6	7653.9541	-0.0010
4	1	4	3	1	3	4304.4180	-0.0042	7	1	6	6	1	5	8409.7402	0.0002
4	0	4	3	0	3	4517.8419	-0.0029	7	0	5	6	2	4	8381.2270	-0.0015
4	1	3	3	1	2	4862.6841	0.0030	7	1	6	6	2	5	7985.5556	-0.0030
4	2	2	3	2	1	4676.5230	0.0048	7	2	7	6	0	6	8175.8719	0.0024
4	2	3	3	2	2	4593.8994	0.0007	7	2	7	6	1	6	6946.4605	0.0049
4	3	1	3	3	0	4618.3385	-0.0026	7	1	6	6	2	5	4582.1597	0.0003
4	3	2	3	3	1	4616.4323	-0.0009	7	0	6	7	0	7	4377.7273	0.0025
4	0	4	3	1	3	3160.8209	0.0134	7	1	5	7	1	6	4350.2385	-0.0009
4	1	4	3	0	3	5661.4550	-0.0046	7	1	6	7	1	7	7259.2296	0.0196
4	1	3	4	0	4	2541.8052	-0.0023	8	2	8	7	1	7	8507.8562	-0.0005
4	2	2	4	1	3	4662.0206	0.0090	8	2	8	7	0	7	8658.3758	-0.0004
4	2	3	4	1	4	5935.5789	0.0005	8	1	7	7	1	6	9552.1978	0.0006
5	1	5	4	1	4	5366.7482	0.0010	8	0	6	7	2	5	9638.2595	-0.0022
5	0	5	4	0	4	5590.2975	-0.0014	8	1	7	7	2	6	9098.9641	0.0027
5	1	4	4	1	3	6060.3106	0.0016	8	2	5	7	3	4	9342.0747	0.0011
5	2	3	4	2	2	5892.0385	-0.0034	8	2	8	7	0	7	9029.7704	-0.0006
5	2	4	4	2	3	5731.8269	-0.0042	8	3	7	7	2	6	6148.8009	0.0030
5	3	2	4	3	1	5783.0340	0.0001	8	1	7	8	0	8	5271.5353	-0.0103
5	3	3	4	3	2	5776.3927	0.0032	8	2	6	8	1	7	4436.3036	-0.0004
5	4	2	4	4	1	5769.3462	-0.0173	9	1	9	8	1	8	9540.6364	-0.0017
5	4	1	4	4	0	5769.3462	-0.0173	9	0	9	8	0	8	9655.5155	-0.0001
5	1	5	4	1	4	4446.6858	0.0017	9	1	8	9	0	9	6282.6835	0.0073
5	0	5	4	0	4	6510.3587	-0.0031	9	2	7	9	1	8	4659.5542	0.0030
5	0	4	5	0	5	3011.8175	-0.0001	10	2	8	10	1	9	5037.7868	-0.0122
								13	3	10	12	4	9	4662.8314	0.0009
								16	3	13	16	2	14	7409.6071	-0.0005

Table S21. Observed rotational transitions and residuals (all the values in MHz) for the D isotopomer of conformer I-w-a of salicylic acid – water complex in the ground vibrational state.

D₁₅

J′	K₋₁′	K₊₁′	J′′	K₋₁′′	K₊₁′′	Obs.	Obs.-Cal.
5	1	5	4	0	4	6463.1357	0.0004
5	1	4	4	1	3	6004.3561	-0.0049
5	2	4	5	1	5	6265.9873	-0.0081
6	0	6	5	0	5	6576.5343	-0.0018
6	1	6	5	1	5	6365.2345	0.0013
6	1	5	5	1	4	7177.6381	-0.0125
6	2	4	5	2	3	7061.7961	-0.0002
6	2	5	5	2	4	6800.7922	-0.0073
6	3	3	5	3	2	6892.1394	0.0101
6	3	4	5	3	3	6875.1162	0.0142
6	2	5	6	1	6	6701.5700	0.0081
7	0	7	6	0	6	7588.2459	-0.0029
7	1	7	6	1	6	7403.2308	0.0054

D₁₆

J′	K₋₁′	K₊₁′	J′′	K₋₁′′	K₊₁′′	Obs.	Obs.-Cal.
5	1	5	4	0	4	6442.8915	-0.0007
5	1	4	4	1	3	6051.2472	-0.0023
5	2	4	5	1	5	6186.9671	0.0023
6	0	6	5	0	5	6606.7178	0.0040
6	1	6	5	1	5	6397.7968	-0.0077
6	1	5	5	1	4	7231.4286	-0.0124
6	2	4	5	2	3	7125.6885	0.0014
6	2	5	5	2	4	6846.3920	0.0076
6	3	3	5	3	2	6945.5148	-0.0022
6	3	4	5	3	3	6926.2226	-0.0005
6	1	6	5	0	5	7270.7137	-0.0018
7	1	7	6	1	6	7439.7925	0.0046
7	0	7	6	1	6	6955.7608	0.0077

D₁₈

J′	K₋₁′	K₊₁′	J′′	K₋₁′′	K₊₁′′	Obs.	Obs.-Cal.
6	0	6	5	0	5	6542.9574	-0.0015
6	1	6	5	1	5	6331.3803	-0.0036
6	1	5	5	1	4	7131.8099	0.0004
6	2	4	5	2	3	7012.0933	-0.0076
6	2	5	5	2	4	6759.8302	-0.0096
6	3	4	5	3	3	6831.5462	0.0121
7	0	7	6	0	6	7551.0337	0.0124
7	1	7	6	1	6	7364.4220	-0.0102
7	3	5	6	3	4	7977.2003	0.0038
7	0	7	6	1	6	6821.1920	0.0024

D₁₉

J′	K₋₁′	K₊₁′	J′′	K₋₁′′	K₊₁′′	Obs.	Obs.-Cal.
5	1	5	4	0	4	6413.6422	-0.0075
6	0	6	5	0	5	6470.7299	-0.0074
6	1	6	5	1	5	6259.9945	-0.0039
6	1	5	5	1	4	7039.3161	-0.0104
6	2	4	5	2	3	6915.0497	-0.0038
6	2	5	5	2	4	6676.2366	0.0077
6	3	3	5	3	2	6758.5973	0.0155
6	1	6	5	0	5	7225.0841	0.0090
6	2	5	6	1	6	6693.1619	0.0005
7	0	7	6	0	6	7469.9648	-0.0110
7	1	7	6	1	6	7282.2478	0.0107

Table S22. Observed rotational transitions and residuals (all the values in MHz) for the I-w₂-a conformer of the salicylic acid –water₂ complex in the ground vibrational state.

J′	K₋₁′	K₊₁′	J′′	K₋₁′′	K₊₁′′	Obs.	Obs.-Cal.	J′	K₋₁′	K₊₁′	J′′	K₋₁′′	K₊₁′′	Obs.	Obs.-Cal.
2	1	2	1	0	1	2850.3823	0.0019	6	1	6	5	1	5	4562.0037	0.0006
2	2	0	1	1	1	5765.3289	-0.0012	6	0	6	5	0	5	4719.5048	-0.0084
2	2	0	2	1	1	3961.1660	0.0145	6	1	5	5	1	4	5099.4890	-0.0009
2	2	1	2	1	2	4229.2841	0.0000	6	2	4	5	2	3	4994.3497	0.0022
3	0	3	2	0	2	2415.5219	-0.0010	6	2	5	5	2	4	4846.8063	0.0048
3	1	3	2	1	2	2294.4946	0.0008	6	3	3	5	3	2	4896.1995	0.0114
3	1	2	2	1	1	2567.0230	0.0008	6	3	4	5	3	3	4888.3418	0.0051
3	1	3	2	0	2	3527.0104	-0.0021	6	4	2	5	4	1	4882.7053	0.0220
3	2	1	2	1	2	6685.4909	-0.0009	6	4	3	5	4	2	4882.5404	-0.0109
3	2	2	2	1	1	6390.2091	0.0002	6	5	1	5	5	0	4878.5206	0.0129
3	2	1	3	1	2	3845.7993	-0.0001	6	5	2	5	5	1	4878.5206	0.0129
3	2	2	3	1	3	4368.3789	-0.0064	6	1	6	5	0	5	5369.6333	0.0030
3	3	1	3	2	2	6824.3537	0.0075	6	1	5	6	0	6	2547.0057	0.0054
4	0	4	3	0	3	3200.0903	0.0024	6	2	4	6	1	5	3481.1254	0.0048
4	1	4	3	1	3	3054.3539	0.0028	6	2	5	6	1	6	5075.6521	0.0010
4	1	3	3	1	2	3417.0610	-0.0006	6	3	3	6	2	4	6611.7643	0.0066
4	2	2	3	2	1	3285.9668	0.0007	6	3	4	6	2	5	6902.2914	-0.0137
4	2	3	3	2	2	3241.2597	-0.0012	7	1	7	6	1	6	5309.0884	0.0037
4	1	4	3	0	3	4165.8406	-0.0001	7	0	7	6	0	6	5454.5611	-0.0019
4	2	2	3	1	3	7676.9481	-0.0158	7	1	6	6	1	5	5927.8315	0.0055
4	2	3	3	1	2	7064.4551	0.0075	7	2	5	6	2	4	5866.6237	-0.0006
4	2	2	4	1	3	3714.6987	-0.0049	7	2	6	6	2	5	5643.2330	-0.0060
4	2	3	4	1	4	4555.2847	-0.0103	7	3	4	6	3	3	5725.1791	0.0033
4	3	2	4	2	3	6836.5240	-0.0125	7	3	5	6	3	4	5707.6929	-0.0003
5	0	5	4	0	4	3968.4742	-0.0017	7	4	3	6	4	2	5701.2278	0.0125
5	1	5	4	1	4	3810.3516	0.0012	7	4	4	6	4	3	5700.7861	0.0092
5	1	4	4	1	3	4261.8374	0.0001	7	5	2	6	5	1	5694.4502	-0.0125
5	2	3	4	2	2	4133.3939	-0.0028	7	5	3	6	5	2	5694.4502	-0.0125
5	2	4	4	2	3	4045.9171	0.0093	7	0	7	6	1	6	4804.4569	0.0109
5	3	2	4	3	1	4073.1045	0.0005	7	1	7	6	0	6	5959.2098	0.0081
5	3	3	4	3	2	4070.1408	-0.0005	7	1	6	6	2	5	2749.0564	-0.0016
5	0	5	4	1	4	3002.7235	0.0003	7	1	6	7	0	7	3020.2674	0.0042
5	1	5	4	0	4	4776.1030	-0.0001	7	2	5	7	1	6	3419.9169	-0.0020
5	2	4	4	1	3	7693.2798	-0.0137	7	2	6	7	1	7	5409.8099	0.0044
5	2	3	5	1	4	3586.2642	0.0010	7	3	4	7	2	5	6470.3153	0.0061
5	2	4	5	1	5	4790.8594	0.0068	8	1	8	7	1	7	6051.6304	0.0015
5	3	2	5	2	3	6709.9106	-0.0066	8	0	8	7	0	7	6177.2483	-0.0108
5	3	3	5	2	4	6860.7894	0.0192	8	1	7	7	1	6	6744.3329	0.0026

Table S22 (Continued).

J′	K₋₁′	K₊₁′	J′′	K₋₁′′	K₊₁′′	Obs.	Obs.-Cal.	J′	K₋₁′	K₊₁′	J′′	K₋₁′′	K₊₁′′	Obs.	Obs.-Cal.
8	2	6	7	2	5	6745.6801	-0.0099	10	1	9	9	2	8	6072.9160	0.0175
8	2	7	7	2	6	6434.5679	-0.0002	10	1	9	10	0	10	4968.8030	0.0078
8	3	5	7	3	4	6561.9892	-0.0171	10	2	8	10	1	9	3671.3362	-0.0116
8	3	6	7	3	5	6527.6079	-0.0011	10	3	7	10	2	8	5835.2668	-0.0088
8	4	4	7	4	3	6522.1184	-0.0083	11	1	11	10	1	10	8255.4204	0.0027
8	4	5	7	4	4	6520.9338	0.0067	11	1	10	10	2	9	7170.4743	-0.0042
8	5	3	7	5	2	6511.7363	-0.0108	11	1	10	11	0	11	5751.2823	-0.0073
8	5	4	7	5	3	6511.7363	-0.0108	11	2	10	11	1	11	7215.8052	0.0054
8	0	8	7	1	7	5672.6052	-0.0153	12	3	9	12	2	10	5404.6643	0.0173
8	1	8	7	0	7	6556.2806	0.0130	13	1	12	13	0	13	7401.9730	0.0061
8	1	7	8	0	8	3587.3315	-0.0026	13	3	10	13	2	11	5257.4606	-0.0043
8	3	5	8	2	6	6286.6271	0.0016	15	3	12	15	2	13	5209.8231	0.0012
8	3	6	8	2	7	7059.8040	0.0036								
9	1	9	8	1	8	6789.8926	-0.0027								
9	0	9	8	0	8	6892.2673	0.0015								
9	1	8	8	1	7	7546.3109	0.0032								
9	2	7	8	2	6	7625.8658	0.0024								
9	2	8	8	2	7	7220.2226	0.0073								
9	3	6	8	3	5	7408.8017	0.0110								
9	3	7	8	3	6	7347.2530	-0.0049								
9	4	5	8	4	4	7345.9653	-0.0128								
9	4	6	8	4	5	7343.1224	0.0033								
9	5	5	8	5	4	7330.5143	-0.0117								
9	6	3	8	6	2	7323.2790	0.0030								
9	6	4	8	6	3	7323.2790	0.0030								
9	0	9	8	1	8	6513.2612	0.0037								
9	1	9	8	0	8	7168.8924	-0.0111								
9	1	8	8	2	7	4961.8785	-0.0103								
9	1	8	9	0	9	4241.3820	0.0058								
9	2	7	9	1	8	3500.8181	-0.0162								
9	2	8	9	1	9	6223.0563	-0.0084								
10	0	10	9	0	9	7603.8071	0.0011								
10	1	10	9	1	9	7524.3052	-0.0086								
10	1	9	9	1	8	8331.2251	0.0001								
10	2	8	9	2	7	8501.7360	-0.0024								
10	2	9	9	2	8	7999.7196	0.0031								
10	0	10	9	1	9	7327.1710	0.0029								
10	1	10	9	0	9	7800.9495	-0.0022								

Table S23. Observed rotational transitions and residuals (all the values in MHz) for the conformer I-w3-a of the salicylic acid –water$_2$ complex in the ground (v=0) and first (v=1) vibrational states.

J'	K$_{-1}$'	K$_{+1}$'	J''	K$_{-1}$''	K$_{+1}$''	v	Obs.	Obs.-Cal.
2	2	1	1	1	0	0	4498.0969	-0.0030
2	2	1	1	1	0	1	4498.0969	-0.0030
3	2	1	2	1	2	0	5194.9698	-0.0185
3	2	1	2	1	2	1	5194.9004	-0.0005
3	2	2	2	1	1	1	5019.6712	0.0028
3	2	2	2	1	1	0	5019.6712	0.0028
3	3	0	2	2	1	0	7351.8188	-0.0010
3	3	0	2	2	1	1	7351.6907	0.0180
3	3	1	2	2	0	0	7349.7515	0.0002
3	3	1	2	2	0	1	7349.6119	0.0073
3	2	1	3	1	2	0	3218.6146	-0.0045
3	2	1	3	1	2	1	3218.5337	0.0074
3	2	2	3	1	3	0	3538.8605	-0.0112
3	2	2	3	1	3	1	3538.7372	0.0022
3	3	0	3	2	1	0	5611.8717	0.0113
3	3	0	3	2	1	1	5611.6807	0.0033
4	0	4	3	0	3	0	2286.4552	0.0042
4	0	4	3	0	3	1	2286.4552	0.0042
4	1	4	3	0	3	0	3160.2814	0.0026
4	1	4	3	0	3	1	3160.2814	0.0026
4	2	3	4	1	4	0	3651.3358	-0.0063
4	2	3	4	1	4	1	3651.1854	0.0055
4	3	2	4	2	3	0	5627.3813	-0.0137
4	3	2	4	2	3	1	5627.2080	-0.0003
5	0	5	4	0	4	0	2843.4585	0.0010
5	0	5	4	0	4	1	2843.5408	0.0103
5	1	5	4	1	4	0	2737.0847	-0.0007
5	1	5	4	1	4	1	2737.0847	-0.0007
5	1	4	4	1	3	0	3011.4643	-0.0009
5	1	4	4	1	3	1	3011.4643	-0.0009
5	2	3	4	2	2	0	2918.2721	-0.0029
5	2	3	4	2	2	1	2918.2721	-0.0029
5	2	4	4	2	3	0	2878.6130	0.0002
5	2	4	4	2	3	1	2878.6730	-0.0044
5	1	5	4	0	4	0	3610.9246	0.0109
5	1	5	4	0	4	1	3610.9246	0.0109
5	2	4	5	1	5	0	3792.8982	0.0085
5	2	4	5	1	5	1	3792.7505	-0.0014
5	3	2	5	2	3	0	5569.8954	0.0108
6	1	6	5	1	5	0	3279.5986	-0.0027
6	1	6	5	1	5	1	3279.7263	0.0020
6	1	5	5	1	4	0	3607.3740	-0.0128
6	1	5	5	1	4	1	3607.4512	-0.0131
6	2	4	5	2	3	0	3518.5406	-0.0033
6	2	5	5	2	4	0	3450.6241	-0.0070
6	2	5	5	2	4	1	3450.6930	-0.0171
6	3	3	5	3	2	0	3472.2202	0.0047
6	3	3	5	3	2	1	3472.2202	0.0047
6	1	6	5	0	5	1	4047.1374	0.0061
6	2	4	6	1	5	0	2949.1094	-0.0035
6	2	5	6	1	6	0	3963.9175	-0.0018
6	2	5	6	1	6	1	3963.7312	-0.0066
6	3	3	6	2	4	0	5523.5388	0.0192
6	3	3	6	2	4	1	5523.3437	-0.0125
7	0	7	6	0	6	0	3931.0615	-0.0017
7	0	7	6	0	6	1	3931.1871	0.0110
7	1	7	6	1	6	0	3819.8589	-0.0009
7	1	7	6	1	6	1	3819.9899	0.0057
7	1	6	6	1	5	0	4199.5088	-0.0162
7	1	6	6	1	5	1	4199.5876	-0.0097
7	2	5	6	2	4	0	4125.8391	0.0015
7	2	5	6	2	4	1	4125.8391	0.0015
7	3	4	6	3	3	0	4056.1818	0.0019
7	3	4	6	3	3	1	4056.1818	0.0019
7	3	5	6	3	4	0	4050.3505	-0.0022
7	3	5	6	3	4	1	4050.4368	-0.0016
7	5	2	6	5	1	1	4043.6532	-0.0014
7	5	3	6	5	2	1	4043.6532	-0.0014
7	0	7	6	1	6	0	3275.8068	0.0079
7	0	7	6	1	6	1	3275.9063	-0.0003
7	1	7	6	0	6	1	4475.2660	0.0124
7	2	5	7	1	6	0	2875.3619	-0.0008
7	2	5	7	1	6	1	2875.3619	-0.0008
7	2	6	7	1	7	0	4164.7058	0.0016
7	2	6	7	1	7	1	4164.4981	0.0048
7	3	4	7	2	5	0	5453.8508	-0.0047

Table S23 (Continued).

J′	K₋₁′	K₊₁′	J″	K₋₁″	K₊₁″	v	Obs.	Obs.-Cal.	J′	K₋₁′	K₊₁′	J″	K₋₁″	K₊₁″	v	Obs.	Obs.-Cal.
7	3	4	7	2	5	1	5453.6964	-0.0083	9	1	9	8	0	8	0	5333.0471	-0.0027
7	3	5	7	2	6	0	5687.0288	-0.0132	9	1	9	8	0	8	1	5333.2402	0.0066
7	3	5	7	2	6	1	5686.8413	0.0028	10	0	10	9	0	9	0	5505.8622	-0.0075
8	0	8	7	0	7	0	4462.0436	0.0035	10	0	10	9	0	9	1	5506.0474	-0.0020
8	0	8	7	0	7	1	4462.1763	0.0013	10	1	10	9	1	9	0	5426.6261	-0.0086
8	1	8	7	1	7	0	4357.7494	-0.0003	10	1	10	9	1	9	1	5426.6261	-0.0086
8	1	8	7	1	7	1	4357.8974	0.0061	10	1	9	9	1	8	0	5942.2026	0.0006
8	2	6	7	2	5	0	4738.9407	-0.0021	10	1	9	9	1	8	1	5942.3107	-0.0056
8	2	6	7	2	5	1	4739.0235	-0.0022	10	3	7	9	3	6	0	5829.9987	0.0025
8	2	7	7	2	6	0	4588.3474	0.0062	10	3	7	9	3	6	1	5830.1140	0.0077
8	2	7	7	2	6	1	4588.4661	0.0091	10	0	10	9	1	9	0	5159.1060	-0.0012
8	3	5	7	3	4	0	4643.1704	-0.0048	10	0	10	9	1	9	1	5159.2556	-0.0050
8	3	5	7	3	4	1	4643.2797	0.0108	10	1	10	9	0	9	0	5773.3106	0.0034
8	3	6	7	3	5	0	4631.7135	0.0092	10	1	9	9	1	8	0	5942.2023	0.0004
8	3	6	7	3	5	1	4631.8139	0.0121	10	1	9	9	1	8	1	5942.3102	-0.0061
8	0	8	7	1	7	0	3917.9794	0.0002	10	3	7	9	3	6	0	5829.9982	0.0020
8	0	8	7	1	7	1	3918.0947	-0.0027	10	3	7	9	3	6	1	5830.1138	0.0075
8	1	8	7	0	7	0	4901.8099	-0.0007	11	0	11	10	0	10	0	6022.8168	0.0003
8	1	8	7	0	7	1	4901.9630	-0.0057	11	0	11	10	0	10	1	6023.0202	0.0020
8	2	6	8	1	7	0	2827.5036	-0.0112	11	1	11	10	1	10	0	5957.7224	0.0083
8	2	6	8	1	7	1	2827.5036	-0.0112	11	1	11	10	1	10	1	5957.9005	-0.0135
8	2	7	8	1	8	0	4395.3123	0.0168	11	1	10	10	1	9	0	6507.9718	0.0042
8	2	7	8	1	8	1	4395.0584	-0.0005	11	1	10	10	1	9	1	6508.0954	-0.0052
8	3	5	8	2	6	0	5358.0903	0.0023	11	2	9	10	2	8	0	6591.6859	0.0041
8	3	5	8	2	6	1	5357.9308	-0.0171	11	3	8	10	3	7	1	6431.7558	0.0035
9	0	9	8	0	8	0	4986.2897	0.0023	11	3	9	10	3	8	0	6376.2692	-0.0048
9	0	9	8	0	8	1	4986.4408	-0.0039	11	3	9	10	3	8	1	6376.4084	-0.0003
9	1	9	8	1	8	0	4893.2757	-0.0034	11	0	11	10	1	10	1	5755.5525	-0.0015
9	1	9	8	1	8	1	4893.4389	-0.0008	11	1	11	10	0	10	0	6225.1607	0.0092
9	1	8	8	1	7	0	5368.0884	0.0068	11	1	11	10	0	10	1	6225.3710	-0.0072
9	1	8	8	1	7	1	5368.1716	-0.0078	12	0	12	11	0	11	1	6538.9550	-0.0096
9	2	7	8	2	6	0	5355.9481	0.0024	12	0	12	11	0	11	0	6538.7405	-0.0009
9	2	7	8	2	6	1	5356.0761	-0.0013	12	1	12	11	1	11	0	6487.0078	0.0020
9	2	8	8	2	7	0	5153.4320	0.0033	12	1	12	11	1	11	1	6487.2333	-0.0006
9	2	8	8	2	7	1	5153.6041	0.0011	12	2	10	11	2	9	1	7205.7509	-0.0006
9	3	6	8	3	5	1	5234.2430	-0.0083	12	2	11	11	2	10	0	6830.6052	-0.0017
9	3	7	8	3	6	0	5213.3825	-0.0039	12	2	11	11	2	10	1	6830.7892	-0.0004
9	3	7	8	3	6	1	5213.4955	-0.0002	12	1	12	11	0	11	1	6689.5912	0.0051
9	4	6	8	4	5	0	5208.7158	-0.0001	13	0	13	12	0	12	0	7054.7088	0.0024
9	4	6	8	4	5	1	5208.8316	0.0059	13	0	13	12	0	12	1	7054.9563	0.0058
9	0	9	8	1	8	0	4546.5049	-0.0118	13	1	12	12	1	11	1	7610.9945	-0.0049
9	0	9	8	1	8	1	4546.6503	-0.0005									

Table S24. Observed rotational transitions and residuals (all the values in MHz) for the conformer I-w$_4$-a of the salicylic acid –water$_2$ complex in the ground vibrational state.

J′	K$_{-1}$′	K$_{+1}$′	J′′	K$_{-1}$′′	K$_{+1}$′′	Obs.	Obs.-Cal.	J′	K$_{-1}$′	K$_{+1}$′	J′′	K$_{-1}$′′	K$_{+1}$′′	Obs.	Obs.-Cal.
3	1	3	2	0	2	2146.8089	-0.0062	7	1	7	6	0	6	3751.3734	0.0006
3	3	0	2	2	1	5513.9673	0.0132	7	2	6	6	1	5	5460.7957	-0.0084
3	3	1	2	2	0	5513.2546	-0.0077	7	3	4	6	2	5	7409.6071	-0.0009
4	1	4	3	0	3	2562.6496	-0.0015	7	3	5	6	2	4	7360.3244	0.0022
4	3	1	3	2	2	5984.4313	0.0017	7	3	4	7	2	5	4047.5752	0.0048
4	3	2	3	2	1	5980.9664	0.0137	7	3	5	7	2	6	4129.1939	0.0114
4	3	1	4	2	2	4098.4762	-0.0011	8	0	8	7	0	7	3698.5373	0.0051
4	3	2	4	2	3	4108.5900	-0.0009	8	1	8	7	1	7	3630.9163	0.0220
5	0	5	4	0	4	2331.8498	-0.0033	8	1	7	7	1	6	3846.7699	-0.0109
5	1	4	4	1	3	2410.5358	-0.0024	8	2	6	7	2	5	3798.1278	0.0129
5	2	3	4	2	2	2357.3344	-0.0054	8	2	7	7	2	6	3744.2092	0.0129
5	2	4	4	2	3	2343.8449	-0.0008	8	3	5	7	3	4	3762.0754	0.0030
5	1	5	4	0	4	2967.3543	0.0025	8	3	6	7	3	5	3759.4316	0.0054
5	3	2	4	2	3	6456.4877	-0.0052	8	5	3	7	5	2	3755.9425	0.0005
5	3	3	4	2	2	6446.0107	0.0027	8	5	4	7	5	3	3755.9425	0.0005
5	3	2	5	2	3	4088.9710	0.0058	8	0	8	7	1	7	3193.7919	0.0066
5	3	3	5	2	4	4112.3457	-0.0043	8	1	8	7	0	7	4135.6564	-0.0137
6	0	6	5	0	5	2791.0225	-0.0003	8	2	7	7	1	6	5835.5772	0.0037
6	1	6	5	1	5	2727.3138	-0.0008	8	3	5	7	2	6	7893.4910	-0.0019
6	1	5	5	1	4	2890.5948	0.0004	8	4	5	7	4	4	3757.3312	0.0055
6	2	4	5	2	3	2834.7346	0.0015	8	3	5	8	2	6	4011.4997	-0.0006
6	2	5	5	2	4	2811.3499	-0.0051	8	3	6	8	2	7	4144.4075	-0.0060
6	3	3	5	3	2	2818.4821	-0.0011	9	0	9	8	0	8	4146.8516	0.0033
6	3	4	5	3	3	2817.8846	-0.0056	9	1	9	8	1	8	4081.2990	-0.0003
6	1	6	5	0	5	3362.8182	0.0049	9	1	8	8	1	7	4322.2770	0.0125
6	3	3	5	2	4	6931.1303	-0.0001	9	2	7	8	2	6	4283.9072	0.0092
6	3	4	5	2	3	6906.5580	-0.0004	9	2	8	8	2	7	4209.3349	-0.0125
6	3	3	6	2	4	4072.7183	0.0028	9	3	6	8	3	5	4235.4439	-0.0125
6	3	4	6	2	5	4118.8850	-0.0002	9	3	7	8	3	6	4230.6017	0.0109
7	0	7	6	0	6	3246.6293	-0.0033	9	4	5	8	4	4	4228.2264	0.0081
7	1	7	6	1	6	3179.5783	0.0001	9	4	6	8	4	5	4228.1088	-0.0016
7	1	6	6	1	5	3369.4318	-0.0004	9	5	4	8	5	3	4226.1287	-0.0010
7	2	5	6	2	4	3314.9854	-0.0013	9	5	5	8	5	4	4226.1287	-0.0010
7	2	6	6	2	5	3278.1774	-0.0021	9	6	3	8	6	2	4225.0956	-0.0054
7	3	4	6	3	3	3289.8309	-0.0014	9	6	4	8	6	3	4225.0956	-0.0054
7	3	5	6	3	4	3288.5017	0.0002	9	0	9	8	1	8	3709.7226	0.0015
7	4	3	6	4	2	3286.9172	0.0061	9	1	9	8	0	8	4518.4211	-0.0108
7	4	4	6	4	3	3286.9172	0.0061	9	2	8	8	1	7	6198.1354	0.0026

Table S24 (Continued).

J′	K-1′	K+1′	J′′	K-1′′	K+1′′	Obs.	Obs.-Cal.	J′	K-1′	K+1′	J′′	K-1′′	K+1′′	Obs.	Obs.-Cal.
9	3	6	9	2	7	3963.0512	0.0112	12	0	12	11	1	11	5220.4656	-0.0011
10	0	10	9	0	9	4591.9952	-0.0021	12	1	12	11	0	11	5681.4625	-0.0034
10	1	10	9	1	9	4530.6937	-0.0062	12	2	11	11	1	10	7222.1241	-0.0034
10	1	9	9	1	8	4795.6070	0.0067	13	0	13	12	0	12	5914.8523	0.0005
10	2	8	9	2	7	4771.7779	0.0020	13	1	13	12	1	12	5873.2651	0.0029
10	2	9	9	2	8	4673.4526	-0.0004	13	1	12	12	1	11	6198.5138	-0.0009
10	3	7	9	3	6	4710.2044	0.0091	13	2	11	12	2	10	6240.0009	0.0007
10	3	8	9	3	7	4701.9874	0.0108	13	2	12	12	2	11	6058.8490	-0.0014
10	4	6	9	4	5	4699.4698	-0.0114	13	3	10	12	3	9	6145.8999	0.0077
10	4	7	9	4	6	4699.2522	0.0050	13	3	11	12	3	10	6116.1345	0.0111
10	5	5	9	5	4	4696.5744	0.0115	13	4	9	12	4	8	6116.6417	-0.0073
10	5	6	9	5	5	4696.5744	0.0115	13	4	10	12	4	9	6115.0977	-0.0110
10	6	4	9	6	3	4695.1329	-0.0033	13	5	8	12	5	7	6109.6050	-0.0078
10	6	5	9	6	4	4695.1329	-0.0033	13	5	9	12	5	8	6109.6050	-0.0078
10	0	10	9	1	9	4220.4285	-0.0014	13	6	7	12	6	6	6106.4092	-0.0019
10	1	10	9	0	9	4902.2522	-0.0152	13	6	8	12	6	7	6106.4092	-0.0019
10	3	7	10	2	8	3901.4668	0.0073	13	0	13	12	1	12	5708.6726	-0.0095
10	3	8	10	2	9	4194.2036	-0.0096	13	1	13	12	0	12	6079.4403	0.0085
11	0	11	10	0	10	5034.5708	-0.0035	13	1	12	12	2	11	4710.5208	0.0080
11	1	11	10	1	10	4979.1321	-0.0017	13	2	11	13	1	12	2117.0818	-0.0007
11	1	10	10	1	9	5266.3543	0.0010	13	3	10	13	2	11	3647.4340	0.0065
11	2	9	10	2	8	5260.9964	0.0038	14	0	14	13	0	13	6353.8201	0.0021
11	2	10	10	2	9	5136.4677	-0.0014	14	1	14	13	1	13	6319.0742	-0.0060
11	3	8	10	3	7	5186.6494	0.0026	14	1	13	13	1	12	6659.1514	-0.0095
11	3	9	10	3	8	5173.4379	-0.0015	14	2	12	13	2	11	6728.1741	0.0125
11	4	7	10	4	6	5171.2630	0.0105	14	2	13	13	2	12	6518.0813	0.0069
11	4	8	10	4	7	5170.7828	-0.0029	14	3	11	13	3	10	6629.2689	0.0079
11	5	6	10	5	5	5167.2611	-0.0080	14	3	12	13	3	11	6587.0546	0.0085
11	5	7	10	5	6	5167.2611	-0.0080	14	4	10	13	4	9	6590.5007	-0.0121
11	7	4	10	7	3	5164.2731	0.0083	14	5	9	13	5	8	6581.2954	-0.0121
11	7	5	10	7	4	5164.2731	0.0083	14	6	8	13	6	7	6577.2972	0.0104
11	0	11	10	1	10	4724.2990	-0.0053	14	6	9	13	6	8	6577.2972	0.0104
11	1	11	10	0	10	5289.4113	0.0073	14	1	14	13	0	13	6483.6656	0.0054
11	2	10	10	1	9	6890.1814	-0.0052	15	0	15	14	0	14	6792.6297	0.0103
11	3	9	11	2	10	4231.1812	-0.0023	15	1	15	14	1	14	6764.1666	-0.0023
12	0	12	11	0	11	5475.2903	-0.0060	15	2	13	14	2	12	7214.5289	-0.0011
12	1	12	11	1	11	5426.6261	-0.0103	15	3	12	14	3	11	7115.3710	-0.0115
12	1	11	11	1	10	5734.1331	0.0074	15	3	13	14	3	12	7057.4591	-0.0135
12	2	10	11	2	9	5750.6893	0.0019	16	0	16	15	0	15	7231.5346	0.0059
12	2	11	11	2	10	5598.2924	-0.0016	16	1	16	15	1	15	7208.6075	-0.0039
12	3	9	11	3	8	5665.1083	-0.0006	16	1	15	15	1	14	7568.3080	-0.0055
12	3	10	11	3	9	5644.8739	0.0048	16	5	11	15	5	10	7526.0149	-0.0085
12	4	8	11	4	7	5643.5959	-0.0132	16	5	12	15	5	11	7525.7635	0.0047
12	4	9	11	4	8	5642.7359	-0.0019	16	1	16	15	0	15	7310.0003	-0.0028
12	5	7	11	5	6	5638.2794	0.0031	17	0	17	16	0	16	7670.6928	-0.0017
12	5	8	11	5	7	5638.2794	0.0031								